

**HANDBOOK**  
*of*  
**BASIC TABLES**  
*for*  
**CHEMICAL**  
**ANALYSIS**  
*Second Edition*

**Thomas J. Bruno**  
**Paris D.N. Svoronos**



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# Dedication

*We dedicate this work to our children, Kelly-Anne, Alexandra, and Theodore.*

## Preface to the First Edition

This work began as a slim booklet prepared by one of the authors (T.J.B.) to accompany a course on chemical instrumentation presented at the National Institute of Standards and Technology, Boulder Laboratories. The booklet contained tables on chromatography, spectroscopy, and chemical (wet) methods, and was intended to provide the students with enough basic data to design their own analytical methods and procedures. Shortly thereafter, with the co-authorship of Professor Paris D.N. Svoronos, it was expanded into a more extensive compilation entitled *Basic Tables for Chemical Analysis*, published as a National Institute of Standards and Technology Technical Note (number 1096). That work has now been expanded and updated into the present body of tables.

Although there have been considerable changes since the first version of these tables, the aim has remained essentially the same. We have tried to provide a single source of information for those practicing scientists and research students who must use various aspects of chemical analysis in their work. In this respect, it is geared less toward the researcher in analytical chemistry than to those practitioners in other chemical disciplines who must make routine use of chemical analysis. We have given special emphasis to those “instrumental techniques” that are most useful in solving common analytical problems. In many cases, the tables contain information gleaned from the most current research papers, and provide data not easily obtainable elsewhere. In some cases, data are presented that are not available at all in other sources. An example is the section covering supercritical fluid chromatography, in which a tabular P- $\rho$ -T surface for carbon dioxide has been calculated (specifically for this work) using an accurate equation of state.

While the authors have endeavored to include data, which they perceive to be most useful, there will undoubtedly be areas that have been slighted. We therefore ask you, the user, to assist us in this regard by informing the corresponding author (T.J.B.) of any topics or tables that should be included in future editions.

The authors acknowledge some individuals who have been of great help during the preparation of this work. Stephanie Outcalt and Juli Schroeder, chemical engineers at the National Institute of Standards and Technology, provided invaluable assistance in searching the literature and compiling a good deal of the data included in this book. Teresa Yenser, manager of the NIST word processing facility, provided excellent copy despite occasional disorganization on the part of the authors. We owe a great debt to our board of reviewers, who provided insightful comments on the manuscript: Profs. D.W. Armstrong, S. Chandrasegaran, G.D. Christian, D. Crist, C.F. Hammer, K. Nakanishi, C.F. Poole, E. Sarlo, Drs. R. Barkley, W. Egan, D.G. Friend, S. Ghayourmanesh, J.W. King, M.L. Loftus, J.E. Mayrath, G.W.A. Milne, R. Reinhardt, R. Tatken, and D. Wingelet. The authors acknowledge the financial support of the Gas Research Institute and the United States Department of Energy, Office of Basic Energy Sciences (T.J.B.) and the National Science Foundation, and the City University of New York (P.D.N.S.). Finally, we must thank our wives, Clare and Soraya, for their patience throughout the period of hard work and late nights.



## Preface to the Second Edition

Some 15 years have elapsed since the publication of the first edition of the *CRC Handbook of Basic Tables for Chemical Analysis*. Since that time, many advances have taken place in the fields of chemical analysis. Because of these advances, the second edition is considerably expanded from the first. We consider this revision unique in that it features to a large extent the input of users of the first edition. In the preface of the first edition, we requested that users contact us with suggestions and additions for the present volume. Over the years, we have gotten many excellent suggestions, for which we are grateful. In many respects, this volume is a result of user input, as well as the efforts of researchers in analytical chemistry who have advanced the field. The user will find in this volume many new tables and several new chapters. We have added a chapter on electrophoresis and one on electroanalytical methods. The section on gas chromatography has been expanded to include the modern methods of solid phase microextraction (SPME) and head space analysis in general, and also new information on detector optimization. The stationary phase tables have been revised. We have deliberately chosen to leave information of historical significance. Thus, while many of the gas chromatographic stationary phases presented for packed columns are not often used today, inclusion of such information in this volume will make it easier to interpret the literature. The section on high-performance liquid chromatography has been updated with the most recent chiral stationary phases, detector information, and revised solvent tables. The tables on spectroscopy have been significantly expanded as well, and in some cases, we have adopted different presentation formats that we hope will be more useful. The miscellaneous tables present in the first edition have been expanded and have in fact spawned two new chapters: "Solutions Properties" and "Tables for Laboratory Safety." In "Solution Properties," we collect in one place information on organic and inorganic solvents and mixtures used in chemical analysis. Reflecting the growing emphasis on laboratory safety, this topic is now treated far more in depth in "Tables for Laboratory Safety." We provide information on many kinds of chemical hazards and electrical hazards in the analytical laboratory, and information to aid the user in selecting laboratory gloves, apparel, and respirators. This aspect of the book is unique, since no other handbook of analytical chemistry provides a self-contained source of information that covers not only carrying out a lab procedure, but also carrying it out safely.

Our philosophy in preparing this book has been to include information that will help the user make decisions. In this respect, we envision each table to be something the user will consult when reaching a decision point in designing an analysis or interpreting results. We have deliberately chosen to exclude information that is merely interesting, but of little value at a decision point.

Similarly, it has occasionally been difficult to strike an appropriate balance between presenting information that is of general utility and information that is highly specific and perhaps simply a repetition of what is contained in vendor catalogs, promotional brochures, and websites. In this respect, we have tried to keep the content as generic and unbiased as possible. Thus, some specific chromatographic phases and columns, available only under trade names, have been excluded. This must not be regarded as a value judgment, but simply a reflection of our philosophy.

## Acknowledgments

The authors acknowledge some individuals who have been of great help during the preparation of this work. Marilyn Yetzbacher of NIST prepared the artwork used throughout this volume. Lorene Celano, also of NIST, prepared many of the tables in the revision. Without the help of these two individuals, this volume could never have been completed. As before, we owe a great debt to our board of reviewers: Profs. M. Jensen, A.F. Lagalante, D.C. Locke, K.E. Miller, Drs. W.C. Andersen, D.G. Friend, S. Ghayourmanesh, A.M. Harvey, M.L. Huber, D. Joshi, M.O. McLinden, S. Ringen, S. Rudge, M.M. Schantz, and D. Smith. Finally, we must again thank our wives, Clare and Soraya, and our children, Kelly-Anne, Alexandra, and Theodore, for their patience and support throughout the period of hard work and late nights.

## The Authors

**Thomas J. Bruno, Ph.D.**, is a project leader in the Physical and Chemical Properties Division at the National Institute of Standards and Technology, Boulder, CO. He is also on the adjunct faculty in the Department of Chemical Engineering at the Colorado School of Mines. Dr. Bruno received his B.S. in chemistry from the Polytechnic Institute of Brooklyn, and his M.S. and Ph.D. in physical chemistry from Georgetown University. He served as a National Academy of Sciences–National Research Council postdoctoral associate at NIST, and was later appointed to the staff. Dr. Bruno has done research on properties of fuel mixtures, chemically reacting fluids, and environmental pollutants. He is also involved in research on supercritical fluid extraction and chromatography of bioproducts, the development of novel analytical methods for environmental contaminants and alternative refrigerants, and novel detection devices for chromatography, and he manages the division analytical chemistry laboratory. In his research areas, he has published approximately 115 papers and 5 books and holds 10 patents. He was awarded the Department of Commerce Bronze Medal in 1986 for his work on the thermophysics of reacting fluids. He has served as a forensic consultant and an expert witness for the U.S. Department of Justice (DOJ), and received in 2002 a letter of commendation from the DOJ for these efforts.

**Paris D.N. Svoronos, Ph.D.**, is professor of chemistry and department chair at QCC of the City University of New York. In addition, he holds a continuing appointment as visiting professor in the Department of Chemistry at Georgetown University. Dr. Svoronos obtained a B.S. in chemistry and a B.S. in physics at the American University of Cairo, and his M.S. and Ph.D. in organic chemistry at Georgetown University. Among his research interests are synthetic sulfur and natural product chemistry, organic electrochemistry, and organic structure determination and trace analysis. He also maintains a keen interest in chemical education and has authored several widely used laboratory manuals used at the undergraduate levels. In his fields of interest, he has approximately 70 publications. He has been in the *Who's Who of America's Teachers* three times in the last five years. He is particularly proud of his students' successes in research presentations, paper publications, and professional accomplishments. He was selected as the 2003 Professor of the Year by the CASE (Council for the Advancement and Support of Education) committee of the Carnegie Foundation.

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## CHAPTER 1

# Gas Chromatography

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## CARRIER GAS PROPERTIES

The following table gives the properties of common gas chromatographic carrier gases. These properties are those used most often in designing separation and optimizing detector performance. The density values are determined at 0°C and 0.101 MPa (760 torr).<sup>1</sup> The thermal conductivity values,  $\lambda$ , are determined at 48.9°C (120°F).<sup>1</sup> The viscosity values are determined at the temperatures listed and at 0.101 MPa (760 torr).<sup>1</sup> The heat capacity (constant pressure) values are determined at 15°C and 0.101 MPa (750 torr).<sup>2</sup>

## REFERENCES

1. Lide, D.R., Ed., *Handbook of Chemistry and Physics*, 83rd ed., CRC Press, Boca Raton, FL, 2002.
2. Dal Nogare, S. and Juvet, R.S., *Gas-Liquid Chromatography: Theory and Practice*, John Wiley & Sons (Interscience), New York, 1962.

Carrier Gas Properties								
Carrier Gas	Density (kg/m <sup>3</sup> )	Thermal Conductivity × 10 <sup>-2</sup> , W/(m·K)	Thermal Conductivity Differences, W/(m·K)			Viscosity × 10 <sup>-5</sup> (Pa·s)	Heat Capacity (J/(kg·K))	Relative Molecular Mass
			δλ (He)	δλ (N <sub>2</sub> )	δλ (Ar)			
Hydrogen	0.08988	19.71	3.97	16.96	17.81	0.876 (20.7°C) 1.086 (129.4°C) 1.381 (299.0°C)	14112.7	2.016
Helium	0.17847	15.74	—	12.99	13.84	1.941 (20.0°C) 2.281 (100.0°C) 2.672 (200.0°C)	5330.6	4.003
Methane	0.71680	3.74	-12.00	0.99	1.84	1.087 (20.0°C) 1.331 (100.0°C) 1.605 (200.5°C)	2217.2	16.04
Oxygen	1.42904	2.85	-12.89	0.10	0.95	2.018 (19.1°C) 2.568 (127.7°C) 3.017 (227.0°C)	915.3	32.00
Nitrogen	1.25055	2.75	-12.99	—	0.85	1.781 (27.4°C) 2.191 (127.2°C) 2.559 (226.7°C)	1030.5	28.016
Carbon monoxide	1.25040	2.67	-13.07	-0.08	0.77	1.753 (21.7°C) 2.183 (126.7°C) 2.548 (227.0°C)	1030.7	28.01
Ethane	1.35660	2.44	-13.30	-0.31	0.54	0.901 (17.2°C) 1.143 (100.4°C) 1.409 (200.3°C)	1614.0	30.07
Ethene	1.26040	2.30	-13.44	-0.45	0.40	1.008 (20.0°C) 1.257 (100.0°C) 1.541 (200.0°C)	—	28.05
Propane	2.00960	2.03	-13.71	-0.72	0.13	0.795 (17.9°C) 1.009 (100.4°C) 1.253 (199.3°C)	—	44.09
Argon	1.78370	1.90	-13.84	-0.85	—	2.217 (20.0°C) 2.695 (100.0°C) 3.223 (200.0°C)	523.7	39.94
Carbon dioxide	1.97690	1.83	-13.91	-0.92	-0.07	1.480 (20.0°C) 1.861 (99.1°C) 2.221 (182.4°C)	836.6	44.01
n-butane	2.51900	1.82	-13.92	-0.93	-0.08	0.840 (14.7°C)	—	58.12
Sulfur hexafluoride	650(20°C)	1.63	-14.11	-1.12	-0.27	1.450 (21.1°C)	674.0	146.05

## CARRIER GAS VISCOSITY

The following table provides the viscosity of common carrier gases, in  $\mu\text{Pa}\cdot\text{sec}$ , used in gas chromatography.<sup>1,2</sup> The values were obtained with a corresponding states approach with high-accuracy equations of state for each fluid. Carrier gas viscosity is an important consideration in efficiency and in the interpretation of flow rate data as a function of temperature. In these tables, the temperature,  $T$ , is presented in  $^{\circ}\text{C}$ , and the pressure,  $P$ , is given in kilopascals and in pounds per square inch (absolute). To obtain the gauge pressure (that is, the pressure displayed on the instrument panel of a gas chromatograph), one must subtract the atmospheric pressure. Following the table, the data are presented graphically.

## REFERENCES

1. Lemmon, E.W., Peskin, A.P., McLinden, M.O., and Friend, D.G., *Thermodynamic and Transport Properties of Pure Fluids*, NIST Standard Reference Database 12, Version 5.0, National Institute of Standards and Technology, Gaithersburg, MD, 2000.
2. Lemmon, E.W., McLinden, M.O., and Huber, M.L., *REFPROP, Reference Fluid Thermodynamic and Transport Properties*, NIST Standard Reference Database 23, Version 7, National Institute of Standards and Technology, Gaithersburg, MD, 2002.

**Carrier Gas Viscosity**

T, $^{\circ}\text{C}$	He	H <sub>2</sub>	Ar	N <sub>2</sub>	Air	Ar/CH <sub>4</sub> (90/10)	Ar/CH <sub>4</sub> (95/5)
<b>P = 204.8 kPa, 29.7 psia</b>							
0	18.699	8.3996	20.979	16.655	17.277	20.013	20.505
10	19.163	8.6088	21.625	17.129	17.775	20.625	21.134
20	19.621	8.8154	22.264	17.597	18.266	21.229	21.755
30	20.076	9.0197	22.894	18.058	18.75	21.826	22.369
40	20.527	9.2218	23.517	18.513	19.228	22.415	22.975
50	20.974	9.4216	24.133	18.962	19.699	22.998	23.574
60	21.418	9.6194	24.742	19.404	20.165	23.573	24.166
70	21.858	9.8152	25.344	19.842	20.624	24.142	24.751
80	22.294	10.009	25.939	20.273	21.078	24.705	25.329
90	22.727	10.201	26.527	20.7	21.526	25.261	25.901
100	23.157	10.391	27.109	21.121	21.969	25.811	26.467
110	23.583	10.58	27.685	21.538	22.407	26.355	27.027
120	24.007	10.767	28.255	21.949	22.84	26.893	27.581
130	24.427	10.952	28.819	22.357	23.268	27.426	28.129
140	24.845	11.136	29.378	22.759	23.691	27.953	28.671
150	25.26	11.318	29.931	23.157	24.11	28.474	29.209
160	25.672	11.498	30.479	23.552	24.524	28.991	29.74
170	26.082	11.678	31.021	23.942	24.934	29.502	30.267
180	26.489	11.856	31.558	24.328	25.34	30.008	30.788
190	26.894	12.033	32.09	24.71	25.742	30.51	31.305
200	27.296	12.208	32.618	25.089	26.14	31.006	31.817
210	27.696	12.382	33.14	25.464	26.534	31.499	32.324
220	28.094	12.555	33.658	25.835	26.924	31.986	32.826
230	28.49	12.727	34.172	26.203	27.311	32.47	33.325
240	28.883	12.898	34.681	26.568	27.695	32.949	33.818
250	29.274	13.068	35.186	26.93	28.075	33.424	34.308
260	29.664	13.236	35.687	27.288	28.451	33.894	34.793
270	30.051	13.404	36.183	27.644	28.825	34.361	35.275
280	30.436	13.571	36.676	27.996	29.195	34.824	35.752
290	30.82	13.736	37.164	28.346	29.562	35.284	36.226
300	31.201	13.901	37.649	28.692	29.927	35.739	36.696

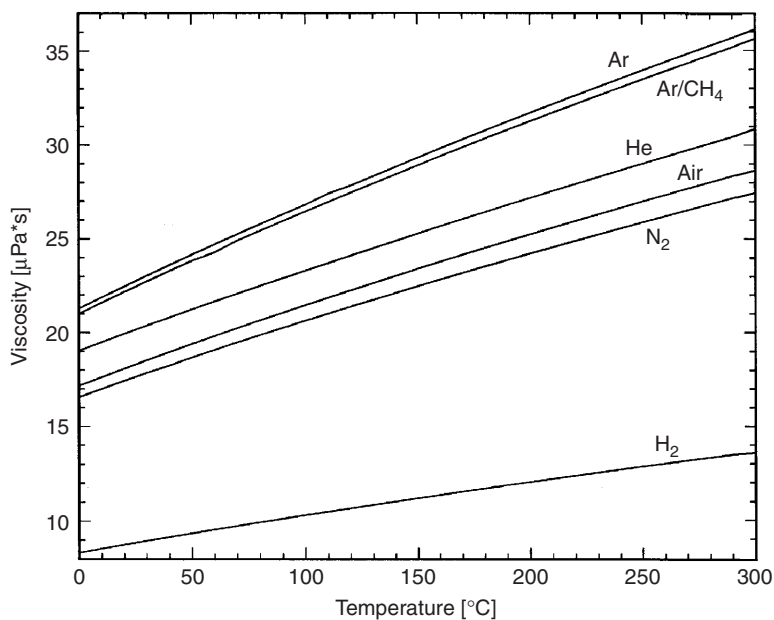


Carrier Gas Viscosity (continued)

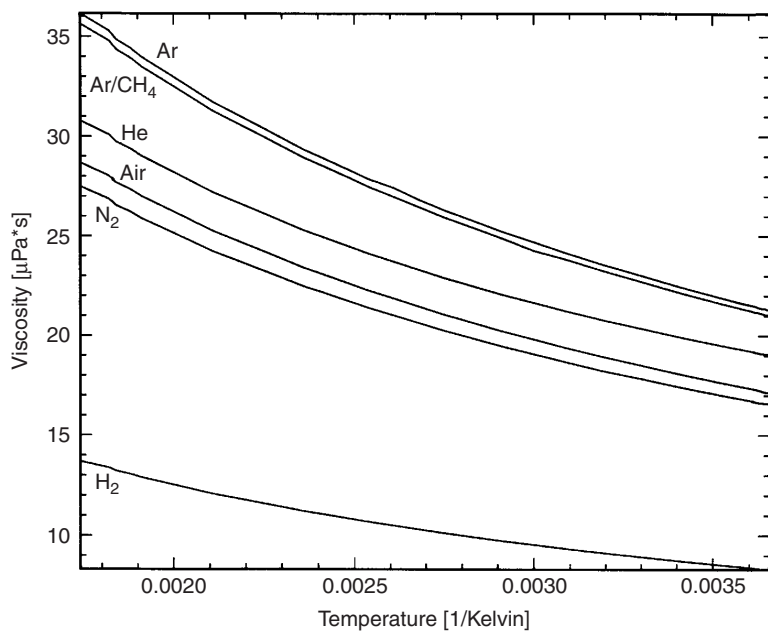
T, °C	He	H <sub>2</sub>	Ar	N <sub>2</sub>	Air	Ar/CH <sub>4</sub> (90/10)	Ar/CH <sub>4</sub> (95/5)
P = 308.2 kPa, 44.7 psia							
0	18.704	8.4024	21.001	16.672	17.296	20.033	20.527
10	19.167	8.6114	21.647	17.146	17.794	20.644	21.155
20	19.625	8.8179	22.285	17.613	18.284	21.248	21.775
30	20.08	9.0222	22.915	18.074	18.767	21.844	22.388
40	20.531	9.2241	23.537	18.528	19.244	22.433	22.993
50	20.978	9.4239	24.152	18.977	19.715	23.015	23.592
60	21.421	9.6217	24.76	19.419	20.18	23.59	24.183
70	21.861	9.8174	25.361	19.856	20.639	24.158	24.768
80	22.297	10.011	25.956	20.287	21.092	24.72	25.346
90	22.73	10.203	26.544	20.713	21.54	25.276	25.917
100	23.159	10.393	27.126	21.134	21.982	25.825	26.483
110	23.586	10.582	27.701	21.55	22.42	26.369	27.042
120	24.009	10.769	28.271	21.962	22.852	26.907	27.596
130	24.43	10.954	28.835	22.369	23.28	27.439	28.143
140	24.847	11.137	29.393	22.771	23.703	27.966	28.685
150	25.262	11.319	29.945	23.169	24.121	28.487	29.222
160	25.675	11.5	30.493	23.563	24.535	29.003	29.754
170	26.084	11.68	31.035	23.953	24.945	29.514	30.28
180	26.491	11.857	31.572	24.338	25.351	30.02	30.801
190	26.896	12.034	32.103	24.72	25.752	30.521	31.317
200	27.298	12.21	32.631	25.099	26.15	31.018	31.829
210	27.698	12.384	33.153	25.474	26.544	31.51	32.336
220	28.096	12.557	33.671	25.845	26.934	31.997	32.838
230	28.492	12.729	34.184	26.213	27.321	32.48	33.336
240	28.885	12.899	34.693	26.577	27.704	32.959	33.829
250	29.276	13.069	35.198	26.939	28.084	33.434	34.319
260	29.666	13.238	35.698	27.297	28.46	33.904	34.804
270	30.053	13.405	36.194	27.652	28.834	34.371	35.285
280	30.438	13.572	36.687	28.005	29.204	34.834	35.763
290	30.822	13.738	37.175	28.354	29.571	35.293	36.236
300	31.203	13.903	37.66	28.701	29.935	35.749	36.706

Carrier Gas Viscosity (continued)

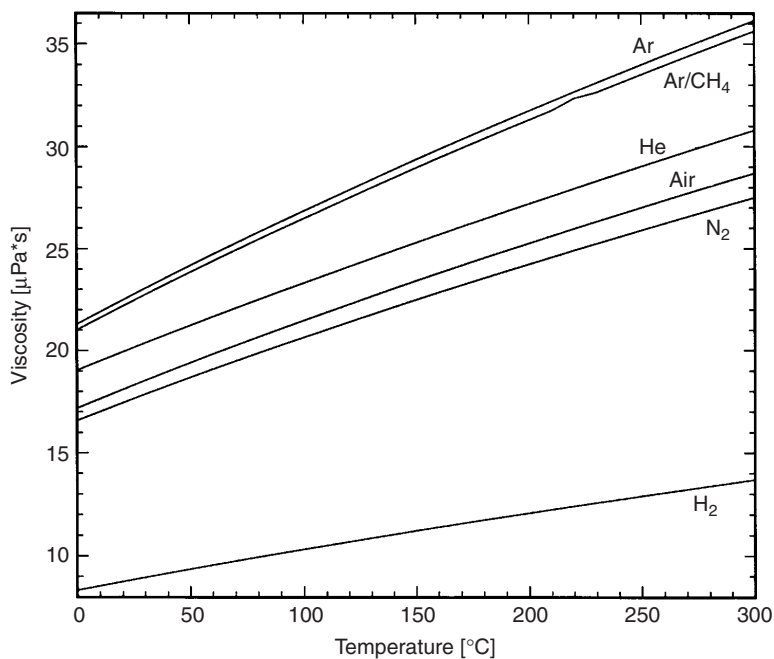
T, °C	He	H <sub>2</sub>	Ar	N <sub>2</sub>	Air	Ar/CH <sub>4</sub> (90/10)	Ar/CH <sub>4</sub> (95/5)
P = 446.1 kPa, 64.7 psia							
0	18.71	8.406	21.032	16.696	17.322	20.061	20.556
10	19.172	8.6149	21.676	17.169	17.818	20.671	21.183
20	19.63	8.8213	22.313	17.636	18.307	21.274	21.802
30	20.085	9.0254	22.942	18.096	18.79	21.869	22.414
40	20.535	9.2273	23.563	18.549	19.266	22.457	23.019
50	20.982	9.427	24.178	18.997	19.736	23.038	23.616
60	21.425	9.6246	24.785	19.439	20.2	23.612	24.207
70	21.865	9.8203	25.385	19.875	20.658	24.18	24.79
80	22.301	10.014	25.979	20.306	21.111	24.741	25.368
90	22.734	10.206	26.567	20.731	21.558	25.296	25.939
100	23.163	10.396	27.148	21.152	22	25.845	26.504
110	23.59	10.584	27.723	21.567	22.437	26.388	27.062
120	24.013	10.771	28.292	21.978	22.869	26.925	27.615
130	24.433	10.956	28.855	22.385	23.296	27.457	28.163
140	24.851	11.14	29.413	22.786	23.719	27.983	28.704
150	25.266	11.322	29.965	23.184	24.137	28.504	29.24
160	25.678	11.502	30.512	23.578	24.55	29.02	29.771
170	26.088	11.682	31.053	23.967	24.96	29.53	30.297
180	26.495	11.86	31.59	24.353	25.365	30.036	30.818
190	26.899	12.036	32.121	24.734	25.766	30.537	31.334
200	27.302	12.212	32.648	25.113	26.164	31.033	31.845
210	27.701	12.386	33.17	25.487	26.557	31.524	32.352
220	28.099	12.559	33.687	25.858	26.947	32.012	32.854
230	28.495	12.731	34.2	26.226	27.334	32.494	33.351
240	28.888	12.901	34.709	26.59	27.717	32.973	33.844
250	29.279	13.071	35.213	26.951	28.096	33.447	34.333
260	29.668	13.24	35.713	27.309	28.472	33.918	34.818
270	30.056	13.407	36.209	27.664	28.845	34.384	35.299
280	30.441	13.574	36.702	28.016	29.215	34.847	35.776
290	30.824	13.74	37.19	28.366	29.582	35.306	36.25
300	31.206	13.904	37.674	28.712	29.946	35.761	36.719



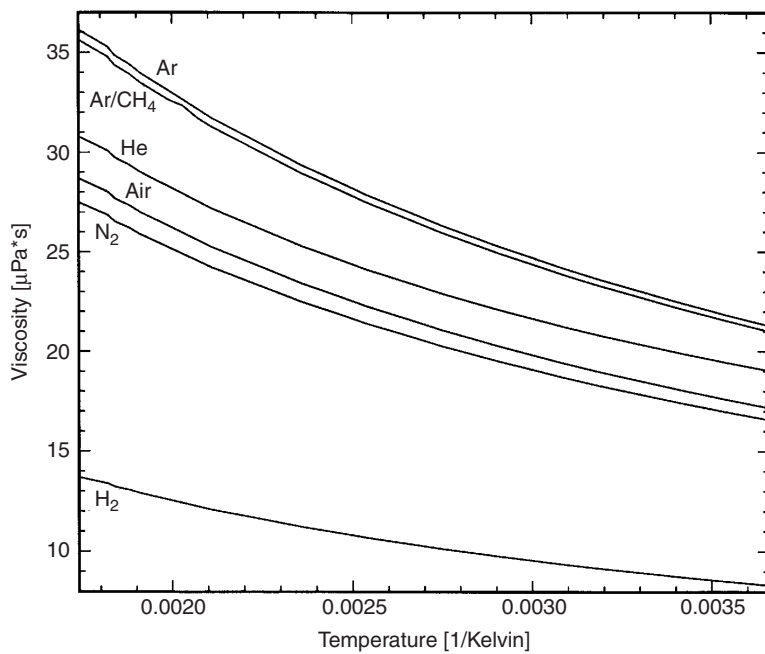
**Figure 1.1** Viscosity vs. temperature at 29.7 psia.



**Figure 1.2** Viscosity vs. temperature at 29.7 psia.



**Figure 1.3** Viscosity vs. temperature at 44.7 psia.



**Figure 1.4** Viscosity vs. temperature at 44.7 psia.

## GAS CHROMATOGRAPHIC SUPPORT MATERIALS FOR PACKED COLUMNS

The following table lists the more common solid supports used in packed column gas chromatography and preparative scale gas chromatography, along with relevant properties.<sup>1-4</sup> The performance of several of these materials can be improved significantly by acid washing and treatment with DMCS (dimethyldichlorosilane) to further deactivate the surface. The nonacid-washed materials can be treated with hexamethyldisilane to deactivate the surface; however, the deactivation is not as great as that obtained by an acid wash followed by DMCS treatment. Most of the materials are available in several particle size ranges. The use of standard sieves will help insure reproducible size packings from one column to the next. Data are provided for the Chromosorb family of supports since they are among the most well characterized. It should be noted that other supports are available to the chromatographer, with a similar range of properties provided by the Chromosorb series.

## REFERENCES

1. Poole, C.F. and Schuette, S.A., *Contemporary Practice of Chromatography*, Elsevier, Amsterdam, 1984.
2. Gordon, A.J. and Ford, R.A., *The Chemist's Companion*, John Wiley & Sons, New York, 1972.
3. Heftmann, E., Ed., *Chromatography: A Laboratory Handbook of Chromatographic and Electrophoretic Methods*, 3rd ed., Van Nostrand Reinhold, New York, 1975.
4. Grant, D.W., *Gas-Liquid Chromatography*, Van Nostrand Reinhold, London, 1971.

**Gas Chromatographic Support Materials for Packed Columns**

<b>Support Name</b>	<b>Support Type</b>	<b>Density (Free Fall), g/ml</b>	<b>Density (Packed), g/ml</b>	<b>pH</b>	<b>Surface Area, m<sup>2</sup>/g</b>	<b>Maximum Liquid Loading</b>	<b>Color</b>	<b>Notes</b>
Chromosorb A	Diatomite	0.40	0.48	7.1	2.7	25%	Pink	Most useful for preparative gas chromatography; high strength; high liquid phase capacity; low surface activity
Chromosorb G	Diatomite	0.47	0.58	8.5	0.5	5%	Oyster white	High mechanical strength; low surface activity; high density
Chromosorb P	Diatomite firebrick	0.38	0.47	6.5	4.0	30%	Pink	High mechanical strength; high liquid capacity; moderate surface activity; for separations of moderately polar compounds
Chromosorb W	Diatomite	0.18	0.24	8.5	1.0	15%	White	Lower mechanical strength than pink supports; very low surface activity; for polar compound separation
Chromosorb 750	Diatomite	0.33	0.49		0.75	7%	White	Highly inert surface; useful for biomedical and pesticide analysis; mechanical strength similar to Chromosorb G
Chromosorb R-4670-1	Diatomite				5–6	Low	White	Ultrafine particle size used to coat inside walls of capillary columns; typical particle size is 1–4 μm
Chromosorb T <sup>a</sup>	Polytetrafluoroethylene	0.42	0.49		7.5	5%	White	Maximum temperature of 240°C; handling is difficult due to static charge; tends to deform when compressed; useful for analysis of high-polarity compounds
Kel-F <sup>a</sup>	Chlorofluorocarbon				2.2	20%	White	Hard, granular chlorofluorocarbon; mechanically similar to Chromosorbs; generally gives poor efficiency; use below 160°C, very rarely used

**Gas Chromatographic Support Materials for Packed Columns (continued)**

<b>Support Name</b>	<b>Support Type</b>	<b>Density (Free Fall), g/ml</b>	<b>Density (Packed), g/ml</b>	<b>pH</b>	<b>Surface Area, m<sup>2</sup>/g</b>	<b>Maximum Liquid Loading</b>	<b>Color</b>	<b>Notes</b>
Fluoropak-80 <sup>a</sup>	Fluorocarbon resin				1.3	5%	White	Granular fluorocarbon with sponge-like structure; low liquid phase capacity; use below 275°C
Teflon-6 <sup>a</sup>	Polytetrafluoroethylene				10.5	20%	White	Usually 40–60 (U.S.) mesh size; for relatively nonpolar liquid phases; low mechanical strength; high inert surface; difficult to handle due to static charge; difficult to obtain good coating of polar phases due to highly inert surface
T-Port-F <sup>a</sup>	Polytetrafluoroethylene	0.5					White	Use below 150°C
Porasil (Types A through F)	Silica				2–500, type dependent	40%	White	Rigid, porous silica bead; controlled pore size varies from 10–150 mm; highly inert; also used as a solid adsorbent

<sup>a</sup> The fluorocarbon supports can be difficult to handle since they develop an electrostatic charge easily. It is generally advisable to work with them below 19°C (solid transition point), using polyethylene laboratory ware.

## MESH SIZES AND PARTICLE DIAMETERS

The following tables give the relationship between particle size diameter (in  $\mu\text{m}$ ) and several standard sieve sizes. The standards are as follows:

United States Standard Sieve Series, ASTM E-11-01

Canadian Standard Sieve Series, 8-GP-16

British Standards Institution, London, BS-410-62

Japanese Standard Specification, JI S-Z-8801

French Standard, AFNOR X-11-501

German Standard, DIN-4188

Mesh Sizes and Particle Diameters					
Particle Size, $\mu\text{m}$	U.S. Sieve Size	Tyler Mesh Size	British Sieve Size	Japanese Sieve Size	Canadian Sieve Size
4000	5	—	—	—	—
2000	10	9	8	9.2	8
1680	12	10	—	—	—
1420	14	12	—	—	—
1190	16	14	—	—	—
1000	18	16	—	—	—
841	20	20	18	20	18
707	25	24	—	—	—
595	30	28	25	28	25
500	35	32	—	—	—
420	40	35	36	36	36
354	45	42	—	—	—
297	50	48	52	52	52
250	60	60	60	55	60
210	70	65	72	65	72
177	80	80	85	80	85
149	100	100	100	100	100
125	120	115	120	120	120
105	140	150	150	145	150
88	170	170	170	170	170
74	200	200	200	200	200
63	230	250	240	250	240
53	270	—	300	280	300
44	325	—	350	325	350
37	400	—	—	—	—



### French and German Sieve Sizes

Particle Size, $\mu\text{m}$	Sieve Size
2000	34
800	30
500	28
400	27
315	26
250	25
200	24
160	23
125	22
100	21
80	20
63	19
50	18
40	17

### Mesh Size Relationships

Mesh Range	Top Screen Opening, $\mu\text{m}$	Bottom Screen Opening, $\mu\text{m}$	Micron Screen, $\mu\text{m}$	Range Ratio
10/20	2000	841	1159	2.38
10/30	2000	595	1405	3.36
20/30	841	595	246	1.41
30/40	595	420	175	1.41
35/80	500	177	323	2.82
45/60	354	250	104	1.41
60/70	250	210	40	1.19
60/80	250	177	73	1.41
60/100	250	149	101	1.68
70/80	210	177	33	1.19
80/100	177	149	28	1.19
100/120	149	125	24	1.19
100/140	149	105	44	1.42
120/140	125	105	20	1.19
140/170	105	88	17	1.19
170/200	88	74	14	1.19
200/230	74	63	11	1.17
230/270	63	53	10	1.19
270/325	53	44	9	1.20
325/400	44	37	7	1.19

## PACKED COLUMN SUPPORT MODIFIERS

During the analysis of strongly acidic or basic compounds, peak tailing is almost always a problem, especially when using packed columns. Pretreatment of support materials, such as acid washing and treatment with DMCS (dimethyldichlorosilane), will usually result in only modest improvement in performance. A number of modifiers can be added to the stationary phase (in small amounts, 1 to 3%) in certain situations to achieve a reduction in peak tailing. The following table provides several such reagents.<sup>1</sup> It must be remembered that the principal liquid phase must be compatible with any modifier being considered. Thus, the use of potassium hydroxide with polyester or polysiloxane phases would be inadvisable, since this reagent can catalyze the depolymerization of the stationary phase. It should also be noted that the use of a tail-reducing modifier may lower the maximum working temperature of a particular stationary phase.

## REFERENCES

1. Poole, C.F. and Schuette, S.A., *Contemporary Practice of Chromatography*, Elsevier, Amsterdam, 1984.

Packed Column Support Modifiers		
Compound Class	Modifier Reagents	Notes
Acids	Phosphoric acid, FFAP (carbowax-20m-terephthalic acid ester), trimer acid	These modifiers will act as subtractive agents for basic components in the sample; FFAP will selectively abstract aldehydes; phosphoric acid may convert amides to the nitrile (of the same carbon number), desulfonate sulfur compounds, and may esterify or dehydrate alcohols
Bases	Potassium hydroxide, polyethyleneimine, polypropyleneimine, <i>N,N'</i> -bis-L-methylheptyl- <i>p</i> -phenylenediamine, sodium metanilate, THEED (tetrahydroxyethylenediamine)	These modifiers will act as subtractive agents for acidic components in the sample; polypropyleneimine will selectively abstract aldehydes, polyethyleneimine will abstract ketones

## PROPERTIES OF CHROMATOGRAPHIC COLUMN MATERIALS

The following table provides physical, mechanical, electrical, and (where appropriate) optical properties of materials commonly used as chromatographic column tubing.<sup>1-6</sup> The data will aid the user in choosing the appropriate tubing material for a given application. The mechanical properties are measured at ambient temperature unless otherwise specified. The chemical incompatibilities cited are usually only important when dealing with high concentrations, which are normally not encountered in gas chromatography. Caution is urged nevertheless.

### REFERENCES

1. *Materials Engineering: Materials Selector*, Penton/IPC, Cleveland, 1986.
2. Khol, R., Ed., *Machine Design*, Materials Reference Issue, 58, 1986.
3. Polar, J.P., *A Guide to Corrosion Resistance*, Climax Molybdenum Co., Greenwich, CT, 1981.
4. Fontana, M.G. and Green, N.D., *Corrosion Engineering*, McGraw-Hill Book Co., New York, 1967.
5. Shand, E.B., *Glass Engineering Handbook*, McGraw-Hill Book Co., New York, 1958.
6. Fuller, A., Corning Glass Works, Science Products Division, Corning, NY, 1988 (private communication).

#### Properties of Chromatographic Column Materials

##### Aluminum (Alloy 3003)

Density	2.74 g/ml
Hardness (Brinell)	28–55
Melting range	643.3–654.4°C
Coefficient of expansion (20–300°C)	$2.32 \times 10^{-5} \text{ }^{\circ}\text{C}^{-1}$
Thermal conductivity (20°C, annealed)	193.14 W/(m·K)
Specific heat (100°C)	921.1 J/(kg·K)
Tensile strength (hard)	152 MPa
Tensile strength (annealed)	110 MPa

*Note:* Soft and easily formed into coils; high thermal conduction; incompatible with strong bases, nitrates, nitrites, carbon disulfide, and diborane.

Actual alloy composition: Mn = 1.5%; Cu = 0.05–0.20%; balance is Al.

##### Copper (Alloy C12200)<sup>a</sup>

Density	8.94 g/ml
Hardness (Rockwell-f)	40–45
Melting point	1082.8°C
Coefficient of expansion (20–300°C)	$1.76 \times 10^{-5} \text{ }^{\circ}\text{C}^{-1}$
Thermal conductivity (20°C)	339.22 W/(m·K)
Specific heat (20°C)	385.11 J/(kg·K)
Tensile strength (hard)	379 MPa
Tensile strength (annealed)	228 MPa
Elongation (in 0.0508 m, annealed) %	45

*Note:* Copper columns often cause adsorption problems; incompatible with amines, anilines, acetylenes, terpenes, steroids, and strong bases.

<sup>a</sup> High-purity phosphorus deoxidized copper.

**Properties of Chromatographic Column  
Materials (continued)**

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Borosilicate Glass	
Density	2.24 g/ml
Hardness (Moh 100)	418
Young's modulus (25°C)	62 GPa
Poisson's ratio (25°C)	0.20
Softening point	806.9°C
Annealing point	565°C
Melting point	1600°C
Strain point	520°C
Coefficient of expansion (average)	$3 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$
Thermal conductivity	1.26 W/(m·K)
Specific heat	710 J/(kg·K)
Refractive index <sup>a</sup>	1.473
Normal service temperature (annealed)	215°C
Extreme service temperature (annealed)	476°C
Critical surface tension	750 mN/m

---

*Note:* Has been used for both packed columns and capillary columns; incompatible with fluorine, oxygen difluoride, and chlorine trifluoride.

<sup>a</sup> Clear grade, at 588 nm.

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Fused Silica (SiO <sub>2</sub> )	
Density	2.15 g/ml
Hardness (Moh)	6
Young's modulus (25°C)	72 GPa
Poisson's ratio (25°C)	0.14
Softening point	1590°C
Annealing point	1105°C
Melting point	1704°C
Strain point	1000°C
Coefficient of expansion (average)	$5 \times 10^{-7} \text{ }^{\circ}\text{C}^{-1}$
Thermal conductivity	1.5 W/(m·K)
Specific heat	1000 J/(kg·K)
Refractive index (588 nm)	1.458
Normal service temperature (annealed)	886°C
Extreme service temperature (annealed)	1086°C
Critical surface tension	760 mN/m

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*Note:* Used for capillary columns; typical inside diameters range from 5 to 530  $\mu\text{m}$ ; coated on outside surface by polyimide or aluminum to prevent surface damage; incompatible with fluorine, oxygen difluoride, chlorine trifluoride, and hydrogen fluoride.

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Nickel (Monel R-405)	
Density	8.83 g/ml
Hardness (Brinell, 21°C)	110–245
Melting range	1298.89–1348.89°C
Coefficient of expansion (21–537°C)	$1.64 \times 10^{-5} \text{ }^{\circ}\text{C}^{-1}$
Thermal conductivity (21°C)	21.81 W/(m·K)
Specific heat (21°C)	427.05 J/(kg·K)
Tensile strength (hard)	483 MPa
Tensile strength (annealed)	793 MPa
Elongation (in 2 in., 21.1°C)	15–50%

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*Note:* Provides excellent corrosion resistance; no major chemical incompatibilities. Actual alloy composition: Ni = 66%; Cu = 31.5%; Fe = 1.35%, C = 0.12%; Mn = 0.9%; S = 0.005%; Si = 0.15%.

### Properties of Chromatographic Column Materials (continued)

Polytetrafluoroethylene (Teflon)	
Specific gravity	2.13–2.24
Hardness (Rockwell-d)	52–65
Melting range	1298.89–1348.89°C
Coefficient of expansion	$1.43 \times 10^{-4} \text{ }^{\circ}\text{C}^{-1}$
Thermal conductivity (21°C)	2.91 W/m·K
Specific heat (21°C)	1046.7 J/kg·K
Tensile strength	17–45 MPa
Refractive index <sup>a</sup>	1.35

*Note:* Flexible and easy to use; cannot be used above 230°C; thermal decomposition products are toxic; tends to adsorb many compounds, which may increase tailing. No major chemical incompatibilities.

<sup>a</sup> Using sodium-D line, as per ASTM standard test D542-50.

Stainless Steel (304)	
Density	7.71 g/ml
Hardness (Rockwell B)	149
Melting range	1398.9–1421.1°C
Coefficient of expansion (0–100°C)	$1.73 \times 10^{-5} \text{ }^{\circ}\text{C}^{-1}$
Thermal conductivity (0°C)	16.27 W/(m·K)
Specific heat (0–100°C)	502.42 J/(kg·K)
Tensile strength (hard)	758 MPa
Tensile strength (annealed)	586 MPa
Elongation (in 2 in.)	60%

*Note:* Good corrosion resistance; easily brazed using silver bearing alloys; high nickel content may catalyze some reactions at elevated temperatures. No major chemical incompatibilities.

Actual alloy composition: C = 0.08%; Mn = 2% (max); Si = 1% (max); P = 0.045% (max); S = 0.030 (max); Cr = 18–20%; Ni = 8–12%, balance is Fe. The low-carbon alloy, 304L, is similar except for C = 0.03% max and is more suitable for applications involving welding operations, and where high concentrations of hydrogen are used.

Stainless Steel (316)	
Density	7.71 g/ml
Hardness (Rockwell B)	149
Melting range	1371.1–1398.9°C
Coefficient of expansion (0–100°C)	$7.17 \times 10^{-5} \text{ }^{\circ}\text{C}^{-1}$
Thermal conductivity (0°C)	16.27 W/(m·K)
Specific heat (0–100°C)	502.42 J/(kg·K)
Tensile strength (annealed)	552 MPa
Elongation (in 2 in.)	60%

*Note:* Best corrosion resistance of any standard stainless steel, including the 304 varieties, especially in reducing and high-temperature environments. Actual alloy composition: C = 0.08% (max), Mn = 2% (max); Si = 1% (max); P = 0.045% (max); S = 0.030 (max); Cr = 16–18%; Ni = 10–14%, Mo = 2–3%, balance is Fe. The low-carbon alloy, 316L, is similar except for C = 0.03% max and is more suitable for applications involving welding operations, and where high concentrations of hydrogen are used.

## PROPERTIES OF SOME LIQUID PHASES FOR PACKED COLUMNS

The following table lists some of the more common gas–chromatographic liquid phases that have been used historically, along with some relevant data and notes.<sup>1–3</sup> Many of these phases have been superseded by silicone phases used in capillary columns, but the liquid phases still find applications in many instances. This is especially true with work involving established protocols, such as ASTM or AOAC methods. Moreover, the data are still useful in interpreting analytical results in the literature. The minimum temperatures, where reported, indicate the point at which some of the phases approach solidification, or when the viscosity increases to the extent that performance is adversely affected. The maximum working temperatures are determined by vapor pressure (liquid phase bleeding) and chemical stability considerations. The liquid phases are listed by their most commonly used names. Where appropriate, chemical names or common generic names are provided in the notes.

The McReynolds constants (a modification of the Rohrschneider constant) tabulated here are based on the retention characteristics of the following test probe samples:

Constant	Test Probe
X	Benzene
Y	1-Butanol
Z	3-Pentanone
U	1-Nitropropane
S	Pyridine

Compounds that are chemically similar to these probe solutes will show similar retention characteristics. Thus, benzene can be thought of as representing lower aromatic or olefinic compounds. Higher values of the McReynolds constant usually indicate a longer retention time (higher retention volume) for a compound represented by that constant, for a given liquid (stationary) phase.

Solvents:	Ace—acetone	MeCl—methylene chloride
	Chlor—chloroform	Tol—toluene
	Pent— <i>n</i> -pentane	MeOH—methanol
	DMP—dimethylpentane	H <sub>2</sub> O—water
	EAC—ethyl acetate	

Polarity:	N—nonpolar
	P—polar
	I—intermediate polarity
	HB—hydrogen bonding
	S—specific interaction

## REFERENCES

1. McReynolds, W.O., Characterization of some liquid-phases, *J. Chromatogr. Sci.*, 8, 685, 1970.
2. McNair, H.M. and Bonelli, E.J., *Basic Gas Chromatography*, Varian Aerograph, Palo Alto, 1968.
3. Heftmann, E., *Chromatography: A Laboratory Handbook of Chromatographic and Electrophoretic Methods*, 3rd. ed., Van Nostrand Reinhold, New York, 1975.

Properties of Some Liquid Phases for Packed Columns

Liquid Phase	T <sub>min</sub> , °C	T <sub>max</sub> , °C	Polarity	Solvents	McReynolds Constant					Notes
					X	Y	Z	U	S	
Acetonyl acetone (2,5-hexanedione)	−4	25	I	Ace					s	
Acetyl tributyl citrate	25	180	I	Ace	135	268	202	314	233	
Adiponitrile	5	50	I	Chlor MeCl						1,4-Dicyanobutane
Alka terge-T, amine surfactant	59	75	I	Chlor MeCl, MeOH						60% oxazoline; weakly cationic
Amine 220	0	180	P	Chlor MeCl	117	380	181	293	133	2-(8-heptadecenyl)-2-imidazoline- ethanol
Ansul ether		80	P	MeOH						Tetraethylene glycol dimethyl ether; used for hydrocarbons
Apiezon H	50	275	N	Chlor	59	56	81	151	129	Low-vapor-pressure hydrocarbon oil
Apiezon J	50	300	N	Chlor MeCl	38	36	27	49	57	Low-vapor-pressure hydrocarbon oil
Apiezon L	50	300	N	Chlor MeCl	32	22	15	32	42	Low-vapor-pressure hydrocarbon oil
Apiezon M	50	275	N	Chlor MeCl	31	22	15	30	40	Low-vapor-pressure hydrocarbon oil
Apiezon N	50	300	N	Chlor MeCl	38	40	28	52	58	Low-vapor-pressure hydrocarbon oil
Apiezon K	50	300+	N	Chlor						Low-vapor-pressure hydrocarbon oil
Apiezon W	50	275	N	Chlor	82	135	99	155	154	Low-vapor-pressure hydrocarbon oil
Apolane-87	30	280	N	Tol	21	10	3	12	35	24,24-diethyl-19,29-dioctadecyl heptatetracontane; C-87 hydrocarbon
Armeen SD		100	P, S, HB	Chlor MeCl						Primary aliphatic amine
Armeen 12D		100	P, HB	Chlor MeCl						
Armeen		125	P, HB	Tol						Secondary aliphatic amine
Armeen 2HT		100	P, HB	Chlor						
Arneel DD		100	P	MeOH						Aliphatic nitrile
Arochlor 1242		125		Ace						Chlorinated polyphenyl; used for gases; may be carcinogenic
Asphalt		300	N	Chlor MeCl						Complex mixture of aliphatic, aromatic, and heterocyclic compounds
Atpet 80			I	Chlor						Sorbitan partial fatty acid esters
<i>p,p</i> -Azoxydiphenetol	130	140	I	Chlor						
Baymal		300		Tol						Colloidal alumina
Beeswax		200		Chlor	43	110	61	88	122	For essential oils
Bentone-34	20	200	S	Tol						Dimethyl dioctadecylammonium bentonite

7,8-Benzoquinoline		150	I	Chlor							For hydrocarbons, aromatics, heterocycles, sulfur compounds
Benzylamine adipate		125		Chlor							
Benzyl cellosolve		50	I	Ace							2-(Benzyloxy ethanol); for hydrocarbons
Benzyl cyanide		50	I	MeOH							Phenyl acetonitrile
Benzyl cyanide-AgNO <sub>3</sub>		25	S	MeCl							
Benzyl diphenyl		100	I	Ace							
Benzyl ether		50	I	Chlor MeCl							Dibenzyl ether
Bis(2-butoxyethyl) phthalate		175	I	MeOH	151	282	227	338	267		
Bis(2-ethoxyethyl) phthalate					214	375	305	446	364		
Bis(2-ethoxyethyl) sebacate					151	306	211	320	274		
<i>N,N</i> -Bis(2-cyanoethyl formamide)	0	125	I	MeOH	690	991	853	110	000		
Bis(2-ethoxyethyl) adipate	0	150	I	Ace							
Bis(2-methoxyethyl) adipate	20	150	I	Ace Chlor							
Bis(2-ethylhexyl) tetrachlorophthalate	0	150	I	Chlor MeCl	112	150	123	108	181		
Butanediol adipate	60	225	I, P	Chlor MeCl							
Butanediol 1,4-succinate		225	I, P	Chlor	370	571	488	651	611		(BDS) craig polyester; for alcohols, aromatics, heterocycles, fatty acids and esters, hydrocarbons
Bis[2-(2-methoxy-ethoxy) ethyl] ether		50	I	Chlor							Tetraethylene glycol dimethylether
Carbitol		100	P	Ace							Glycol ether (molecular mass 134); for aldehydes, ketones
Carbowax 300	10	100	P	MeCl							Polyethylene glycol; average molecular mass <380
Carbowax 400	10	125	P	MeCl	333	653	405				Polyethylene glycol; average molecular mass = 380–420
Carbowax 400 mono-oleate	10	125	P	MeCl							



Properties of Some Liquid Phases for Packed Columns (continued)

Liquid Phase	T <sub>min</sub> , °C	T <sub>max</sub> , °C	Polarity	Solvents	McReynolds Constant					Notes
					X	Y	Z	U	S	
Carbowax 550	20	125	P	MeCl						
Carbowax 600	30	125	P	MeCl	323	583	382			Polyethylene glycol; average molecular mass = 570–630
Carbowax 600 monostearate		125	P	MeCl						
Carbowax 750	25	150	P	MeCl						Methoxy polyethylene glycol; average molecular mass = 715–785
Carbowax 1000	40	175	P	MeCl	347	607	418	626	589	Polyethylene glycol; average molecular mass = 950–1050
Carbowax 1500 (or 540)	40	200	P	MeCl						Polyethylene glycol; average molecular mass = 500–600
Carbowax 1540	40	200	P	MeCl	371	639	453	666	641	Polyethylene glycol; average molecular mass = 1300–1600
Carbowax 4000 (or 3350)	60	200	P	MeCl	317	545	378	578	521	Polyethylene glycol; average molecular mass = 3000–3700
Carbowax 4000 TPA		175	P	MeCl, MeOH						Terminated with terephthalic acid
Carbowax 4000 monostearate	60	220	P	MeCl	282	496	331	517	467	
Carbowax 6000	60	200	P	MeCl	322	540	369	577	512	Polyethylene glycol; average molecular mass = 6000–7500
Carbowax 8000	60	120	P	Chlor	322	540	369	577	512	Polyethylene glycol; average molecular mass = 7000–8500
Carbowax 20M	60	250	P	MeCl	322	536	368	572	510	Polyethylene glycol; average molecular mass = 15,000–20,000
Carbowax 20M-TPA	60	250	P	MeCl	321	537	367	573	520	Terminated with terephthalic acid
Castorwax	90	200	P	MeCl	108	265	175	229	246	Triglyceride of 12-hydroxysteric acid (hydrogenated castor oil)
Citroflex A-4		150	I	MeOH	135	286	213	324	262	Tributyl citrate
Chlorowax 70		130	P	MeCl						Chlorinated paraffin, 70% (w/w) Cl; for hydrocarbons
1-Chloronaphthalene		75	I	Tol						
Cyanoethyl sucrose	20	175	P		647	919	043	976		Vitrifies at –10°C
Cyclodextrin acetate		250	I	Ace						
Cyclohexane	100	210	I	Ace						For fatty acids, esters
dimethanol succinate			I	Chlor	269	446	328	498	481	

<i>n</i> -Decane		30	N	MeCl						For inorganic and organometallic compounds
Di(ethoxyethoxyethyl) phthalate					233	408	317	470	389	
Di(butoxyethyl) adipate	−10	150	P	Ace	137	278	198	300	235	
Di(butoxyethyl) phthalate	−30	200	P	Tol	157	292	233	348	272	
Di- <i>n</i> -butyl cyanamide		50		MeOH						For gases
Di- <i>n</i> -butyl maleate	0	50	P, I	Tol						For halogenated compounds
Di- <i>n</i> -butyl phthalate	−20	100	I	Tol						For aldehydes, ketones, halogenated compounds, hydrocarbons, phosphorus compounds
Dibutyltetrachloro-phthalate	0	150	I	Tol						
Didecyl phthalate	20	150	I	Tol	136	255	213	320	235	
Dicyclohexyl phthalate					146	257	206	316	245	
Diethylene glycol adipate	0	200	I	MeCl	378	603	460	665	658	DEGA; for aldehydes, ketones, esters, fatty acids, pesticides
Diethylene glycol glutarate		225		MeCl						
Diethylene glycol sebacate	80	190	I	MeCl						DEGSB
Diethylene glycol succinate	20	190	P	MeCl	496	746	590	837	835	DEGS; for alcohols, aldehydes, ketones, amino acids, essential oils, steroids, esters, phosphorus and sulfur compounds
Diethylene glycol stearate					64	193	106	143	191	
Di-(2-ethylhexyl) phthalate	20	150	P	Tol	135	254	213	320	235	
Di-(2-ethylhexyl) adipate	−30	250	P	Ace	76	181	121	197	134	Diocetyl adipate
Di-(2-ethylhexyl) sebacate	−20	125	I	Tol	72	168	108	180	125	For alcohols, drugs, alkaloids, esters, fatty acids, halogenated compounds, blood gases
Diethyl-D-tartrate		125	P, S	MeCl						For alcohols

Properties of Some Liquid Phases for Packed Columns (continued)

Liquid Phase	T <sub>min</sub> , °C	T <sub>max</sub> , °C	Polarity	Solvents	McReynolds Constant					Notes
					X	Y	Z	U	S	
Diglycerol	20	120	HB	MeCl, MeOH	371	826	560	676	854	For alcohols, aldehydes, ketones, aromatics, heterocycles, hydrocarbons
Dilauryl phthalate		150	I	Tol	79	158	120	192	158	
Diisodecyl adipate	−10	175	P	Ace	71	171	113	185	128	
Diisooctyl adipate	90	150	P	Ace	78	187	126	204	140	
Diisodecyl phthalate	0	150	I	Tol, Ace	84	173	137	218	155	For alcohols, aromatics, heterocycles, essential oils, esters, halogen and sulfur compounds, hydrocarbons
Diisooctyl sebacate		175	I	Ace						For aldehydes, ketones, hydrocarbons
2,4-Dimethyl sulfolane	0	50	P	Chlor						For hydrocarbons, inorganic and organometallic compounds
Dimer acid		100	I	MeCl						C <sub>36</sub> dicarboxylic acid
Diisooctyl phthalate	0	175	I	Tol	94	193	154	243	202	
Dimethyl formamide	−20	20	P	Ace						DMFs
Dimethyl sulfoxide	20	30	P	MeCl						DMSO; for gases
Dinonyl phthalate	20	150	I	Tol	83	183	147	231	159	For aromatics, heterocycles, halogen compounds
Diocetyl phthalate	−20	150	I	Tol	92	186	150	230	167	For aromatics, heterocycles, halogen compounds
Diocetyl sebacate		100	I	MeCl	72	168	108	180	123	
Diphenyl formamide	75	100	I	Tol						
Di- <i>n</i> -propyl tetrachlorophthalate	10	75	I	Tol						
Ditridecyl phthalate	−10	225	P	Tol	75	156	122	195	140	
Emulphor ON-870	0	200	I	Chlor	202	395	251	395	344	Aryloxy polyethylene oxyethanol; for aromatics, heterocycles, essential oils, halogen compounds
EPON 1001	60	225	P	MeCl (hot)	284	489	406	539	601	Epichlorohydrin-bisphenol A resin; average molecular mass = 900; for steroids, pesticides
Ethofat 60/25	50	125	I	MeCl (hot)	191	382	244	380	333	Polyethylene oxyglycol stearate; for aldehydes, ketones
Ethomeen S/25		75	P	MeCl	186	395	242	370	339	Polyethoxylated aliphatic amine

Ethyl benzoate		150	I	MeOH						For hydrocarbons
Ethylene glycol adipate	100	225	I, P	MeCl	372	576	453	655	617	For alcohols, aromatics, heterocycles, bile/urinary compounds, drugs, alkaloids, essential oils, nitrogen and sulfur compounds
Ethylene glycol phthalate	100	200	I, P	Tol	453	697	602	816	872	For nitrogen compounds, steroids
Ethylene glycol succinate	100	200	I, P	Ace	537	787	643	903	889	
Ethylene glycol glutarate		225	I, P	MeCl						
Ethylene glycol sebacate		200	I, P	MeCl (hot)						
Ethylene glycol tetrachlorophthalate	120	200	P	Tol	307	345	318	428	466	
Ethylene glycol		30	HB	MeOH						
Ethylene glycol silver nitrate		30	S	Ace						
Eutectic (LiNO <sub>3</sub> -NaNO <sub>3</sub> -KNO <sub>3</sub> /27.3–18.2–54.5)		400	—	H <sub>2</sub> O						For aromatic hydrocarbons, heterocycles
Eutectic (KCl-CdCl <sub>2</sub> /33–67)		400	—	H <sub>2</sub> O						For aromatic hydrocarbons, heterocycles
Eutectic (NaCl-AgCl/41–59)		400	—	H <sub>2</sub> O						For aromatic hydrocarbons, heterocycles
Eutectic (BiCl <sub>3</sub> -PbCl <sub>2</sub> /89–11)		400	—	H <sub>2</sub> O						For aromatic hydrocarbons, heterocycles
FFAP	50	250	P, S	Chlor	340	580	397	602	627	Carbowax 20M nitroterephthalic acid ester; for aldehydes, ketones
Flexol 8N8		180	P	Ace	96	254	164	260	179	2,2'-(2-ethyl hexynamido)-diethyl-di-2-ethylhexanoate; for alcohols, nitrogen compounds
Fluorolube HG-1200		100	I	Ace	51	68	114	144	116	Polymers of trifluorovinylchloride; for halogenated compounds
Formamide	20	50	I	MeOH						For alcohols
Glycerol	20	100	HB	MeOH						
Fluorad FC-431	40	200		EAC	281	423	297	509	360	Fluorocarbon surfactant
Hallcomid M-18	40	150	I	MeCl	79	580	397	602	627	Dimethylsteramide; for alcohols, ketones, aldehydes, esters

Properties of Some Liquid Phases for Packed Columns (continued)

Liquid Phase	T <sub>min</sub> , °C	T <sub>max</sub> , °C	Polarity	Solvents	McReynolds Constant					Notes
					X	Y	Z	U	S	
Hallcomid M-18-OL	8	150	I	MeCl	89	280	143	239	165	Dimethyloleamide; for alcohols, ketones, aldehydes, fatty acids
Halocarbon 10-25	20	100	I	Chlor	47	70	108	113	111	
Halocarbon K 352	0	250	I		47	70	73	238	146	
Halocarbon W9X (600)	50	150		Ace	55	71	116	143	123	
Halocarbon-1321	0	100		Ace						Hexamethylphosphoramide
Halocarbon-11-14	0	100		Ace						
HMPA	20	35	P	Chlor						
Hi-Eff-1 AP	20	210	I, P	Chlor	378	603	460	665	658	
Hi-Eff-2 AP	100	210	I, P	Chlor	372	576	453	655	617	Diethyleneglycol adipate
Hi-Eff-8 BB	100	250	I, P	Chlor	271	444	333	498	463	Cyclohexane dimethanol succinate
Hi-Eff-1 BP	20	200	I, P	Chlor	499	751	593	840		Diethylene glycol succinate
Hi-Eff-2 BP	100	200	I, P	Chlor	537	787	643	903	889	Ethylene glycol succinate
Hi-Eff-3 AP	50	230	I, P	Chlor						Neopentyl glycol adipate
Hi-Eff-8 AP	100	250	I, P	Chlor						Cyclohexane dimethanol adipate
Hi-Eff-9 AP	100	250	I, P	Chlor						Tetramethyl cyclobutanediol adipate
Hi-Eff-3 BP			I, P							Neopentyl glycol succinate
Hi-Eff-4 BP	50	230	I, P	Chlor						Butane-1,4-diol succinate
Hi-Eff-10 BP	20	230	I, P	Chlor						Phenyl diethanolamine succinate
Hi-Eff-2 CP	100	200	I, P	Chlor						Ethylene glycol sebacate
Hi-Eff-3 CP	50	230	I, P	Chlor						Neopentyl glycol sebacate
Hi-Eff-2 EP	100	210	I, P	Chlor						Ethylene glycol isophthalate
Hi-Eff-26 P	100	210	I, P	Chlor						Ethylene glycol phthalate
Hyprose-SP-80		225	P	MeOH	336	742	492	639	727	Octakis (2-hydroxy propyl) sucrose
1,2,3,4,5,6-hexakis-(2-cyanoethoxy-cyclohexane)	125	150	I, P	Tol	567	825	713	978	901	
Hercoflex 600		150	P	MeCl	112	234	168	261	194	High boiling ester of pentaerythritol and a saturated aliphatic acid
n-Hexadecane	20	50	N	Pent						Isomeric mixture Cetyl alcohol; for halogenated compounds, hydrocarbons
Hexadecane	20	50	N	Pent						
1-Hexadeconal		35	I	MeOH						
Hexatricontane	80	150	N	MeCl	12	2	-3	1	11	C <sub>36</sub> H <sub>74</sub>

IGEPAL CO-880	100	200	I	MeCl (hot)	259	461	311	482	426	Nonylphenoxy poly(ethyleneoxy-ethanol) n = 30; for alcohols
IGEPAL CO-990	100	200	I	MeCl (hot)	298	508	345	540	475	Nonylphenoxy poly(ethyleneoxy-ethanol); n = 100; for alcohols
IGEPAL CO-630	100	200	I	MeCl (hot)	192	381	253	382	344	Nonylphenoxy poly(ethyleneoxy-ethanol); n = 9; for alcohols
IGEPAL CO-730					224	418	279	428	379	
IGEPAL CO-710	100	200	I		205	397	266	401	361	
$\beta,\beta'$ -iminodipropionitrile		110	I	MeOH						For halogenated compounds
Isoquinoline		50	I, P	MeCl						For hydrocarbons
Lexan	220	270	P	DMP (hot)						Polycarbonate resin
Mannitol	170	200	HB	H <sub>2</sub> O						For sugars
Montan wax		175		Chlor	19	58	14	21	47	For halogenated compounds
Naphthylamine		150	I	Chlor						For aromatics, heterocycles
Neopentylglycol adipate	50	240	I	MeCl	234	425	312	402	438	NPGA; for amino acids, drugs, alkaloids, pesticides, steroids
Neopentylglycol isophthalate	50	240	I	MeCl						
Neopentylglycol sebacate	50	225	I	MeCl	172	327	225	344	326	NPGSB; for amino acids, steroids
Neopentylglycol succinate	50	225	I	MeCl	272	469	366	539	474	NPGS; for amino acids, bile and urinary compounds, esters, inorganics
Nitrobenzene		150	I	MeOH						For hydrocarbons, inorganic and organometallic compounds
Nujol		100	N	Pent	9	5	2	6	11	Paraffin oil, mineral oil; for hydrocarbons
<i>N</i> -Octadecane	30	55	N	Pent						For inorganic and organometallic compounds
Octyl decyl adipate		175		Ace	79	179	119	193	134	
Oronite NIW		170	P		180	370	242	370	327	Complex mixture of petroleum liquids
$\beta,\beta'$ -oxydipropionitrile		100	P	Ace						For halogenated compounds
Phenyl diethanolamine succinate		225	P	Ace	386	555	472	674	654	For drugs, alkaloids, hydrocarbons
Polyethylene imine	0	250	P	MeOH	322	800	—	573	524	
Poly- <i>m</i> -phenylxylene	125	375	I	Tol	257	355	348	433	—	PPE-20
Poly- <i>m</i> -phenyl ether		250	I	Tol	176	227	224	306	283	5 rings; for aromatics, heterocycles

Properties of Some Liquid Phases for Packed Columns (continued)

Liquid Phase	T <sub>min</sub> , °C	T <sub>max</sub> , °C	Polarity	Solvents	McReynolds Constant					Notes
					X	Y	Z	U	S	
Poly- <i>m</i> -phenyl ether	0	300	I	Ace, Tol	182	233	228	313	293	6 rings; for alcohols, essential oils, esters High polymer 6 rings
Poly- <i>m</i> -phenyl ether	50	400	I	Tol						
Poly- <i>m</i> -phenyl ether with squalane	50	100	I	MeCl						
Polypropylene glycol	0	150	HB	MeOH						Average molecular mass = 2000; for drugs, alcohols, alkaloids
Polypropylene glycol sebacate	20	225	I	Chlor	128	294	173	264	226	
Polypropylene glycol silver nitrate	20	75	S	MeCl	196	345	251	381	328	PEG/AgNO <sub>3</sub> -3/1; for unsaturated hydrocarbons
Polypropylene imine	0	200	I, P	Chlor						
Propylene carbonate	0	60	P	MeCl	122	425	168	263	224	1,2-Propanediol cyclic carbonate; for gases, hydrocarbons
Polysulfone	0	315	I	Ace						
Polyvinyl pyrrolidone	80	225	HB	MeOH						<i>N,N,N',N'</i> -Tetrakis (2-hydroxy-propyl); ethylenediamine; for alcohols, aldehydes, ketones, amino acids, essential oils
Quadrol	0	150	HB	Chlor	214	571	357	472	489	
Reoplex 400	0	200	I	MeCl	364	619	449	647	671	Poly(propylene glycol adipate); for aromatics, heterocycles, vitamins, sulfur and phosphorus compounds Poly(propylene glycol sebacate) Ethylene oxide-nonylphenol surfactant; for alcohols
Reoplex 100	0	200	I	MeCl						
Renex-678				MeOH	223	417	278	427	381	
Sebaconitrile		150	P							For hydrocarbons, organic vapors, nitrogen, sulfur and phosphorus compounds
Squalane	20	100	N	Pent	0	0	0	0	0	
Squalene	0	100	N, I	Pent	152	341	238	329	344	For hydrocarbons, gases, nitrogen, sulfur and phosphorus compounds Hexahydric alcohol, C <sub>6</sub> H <sub>6</sub> (OH) <sub>6</sub>
Sorbitol	15	150		Chlor	232	582	313			
STAP	100	255	P	Chlor	345	586	400	610	627	Steroid analysis phase

Siponate-DS-10	20	210	I, P	MeOH						Sodium dodecylbenzene sulfonate
Sorbitan monooleate	20	150	P	Chlor	97	266	170	216	268	SPAN-80
Sorbitol hexaacetate					335	553	449	652	543	
Sucrose acetate isobutyrate	0	200	I, P	MeCl	172	330	251	378	295	SAIB; for alcohols, essential oils
Sucrose octaacetate	90	250	I, P	Ace	344	570	461	671	569	
Tergitol nonionic NP-35	10	175	P	Chlor	197	380	258	389	351	Surfactant mixture
TCEPE	30	175	P, S	MeCl	526	782	677	920	837	Tetracyanoethylated pentaerythritol; for fatty acids, esters
Terephthalic acid	100	250	P, I	Tol						
Tetraethylene glycol		70	P	MeCl						For hydrocarbons
Tetraethylene pent-amine		150	HB	MeOH						For nitrogen compounds
1,2,3,4-Tetrakis-(2-cyanoethyl)butane	110	200	I, P	Chlor	617	860	773	048	941	
THEED	0	125	HB	Chlor	463	942	626	801	893	Tetrahydroxyethylenediamine; for alcohols, hydrocarbons, nitrogen compounds
$\beta,\beta'$ -Thiodipropio-nitrile		100	P	MeOH						For hydrocarbons
Triacetin		60	P	MeOH						For gases
Tributyl phosphate	20	125	I	Ace						For gases
Tricresyl phosphate	20	215	I	MeOH	176	321	250	374	299	Tritolyl phosphate
Triethanolamine		100	HB	MeOH						For alcohols, gases
Trimer acid	20	200	HB	MeOH	94	271	163	182	378	C <sub>54</sub> tricarboxylic acid; for alcohols
1,2,3-Tris(2-cyanoethoxy)propane	30	150	P	MeOH	594	857	759	031	917	For alcohols, aldehydes, ketones, halogen compounds, inorganic and organometallic compounds
Tris(tetrahydrofurfuryl) phosphate	20	125	I	Ace						
Tris(2-cyanoethyl) nitromethane	20	140	I, P	Chlor						
Triton X-100	20	190	P	MeCl	203	399	268	402	362	Octylphenoxy polyethyl ethanol for aromatics, heterocycles
Triton X-305	20	250	P	Ace	262	467	314	488	430	Octylphenoxy polyethyl ethanol for alcohols
Trixylol phosphate	20	250	I, P	Ace						



Properties of Some Liquid Phases for Packed Columns (continued)

Liquid Phase	T <sub>min</sub> , °C	T <sub>max</sub> , °C	Polarity	Solvents	McReynolds Constant					Notes
					X	Y	Z	U	S	
TWEEN-20	20	150	P	MeOH						Polyethoxysorbitan monolaurate; for essential oils
TWEEN-80	20	160	P	MeOH	227	430	283	438	396	Polyethoxysorbitan monooleate; for fatty acids, esters, pesticides
UCON LB-550-X	0	200	P	Chlor	118	271	158	243	206	10% polyethylene glycol, 90% propylene glycol
UCON 50-HB-280-X	0	200	P	Chlor	177	362	227	351	302	30% polyethylene glycol, 70% propylene glycol; for alcohols, fatty acids, esters
UCON 50-HB-2000	0	200	P	Chlor	202	394	253	392	341	40% polyethylene glycol, 60% propylene glycol; for alcohols, aldehydes, ketones
UCON 50-HB-5100	20	200	P	MeCl	214	418	278	421	375	50% polyethylene glycol, 50% propylene glycol
UCON LB-1715	20	200	I	MeCl	132	297	180	275	235	For alcohols, ketones, nitrogen compounds
UCON 75-H-90,000	20	200	P	MeCl	255	452	299	470	406	80% polyethylene glycol, 10% propylene glycol
Versamide 900	190	250	P	MeCl						Polyamide resin; for alcohols
Versamide 940	115	200	P	MeCl	109	314	145	212	209	Polyamide resin; for alcohols
Versamide 930	115	150	P	MeCl	109	313	144	211	209	Polyamide resin
Versamide 940		200	P	See notes	109	314	145	212	209	Soluble in hot chloroform butanol; 50/50 v/v; for aromatics, heterocycles, pesticides, nitrogen compounds
Xylenyl phosphate		175	I	MeCl						
Zonyl E7		200	I	MeCl	223	359	468	549	465	Fluoroalkyl ester
Zonyl E91		200	I	MeCl	130	250	320	377	293	Fluoroalcohol camphorate
Zinc stearate	135	175	I	Ace (warm)	61	231	59	98	544	

## STATIONARY PHASES FOR PACKED COLUMN GAS CHROMATOGRAPHY

The following stationary phases have been of value in the separation of major classes of compounds, using packed columns of typical dimensions (4 to 10 m in length, 0.32 cm in diameter).<sup>1-10</sup> The resolution will undoubtedly be lower than that obtainable with capillary columns, which have superseded packed columns in many applications. The two main exceptions are in the analysis of permanent gases and preparative scale gas chromatography. Data on the packed column stationary phases are included since they still find uses in many laboratories. This table is meant to provide only a rough guide. The additional data that can be found in the preceding stationary phase data table will aid in determining the final choice.

### REFERENCES

1. Heftmann, E., Ed., *Chromatography: A Laboratory Handbook of Chromatographic and Electro-phoretic Methods*, 3rd ed., Van Nostrand Reinhold Co., New York, 1975.
2. Grant, D.W., *Gas-Liquid Chromatography*, Van Nostrand Reinhold Co., London, 1971.
3. McNair, H.M. and Bonelli, E.J., *Basic Gas Chromatography*, Varian Aerography, Palo Alto, CA, 1969.
4. Grob, R.L., Ed., *Modern Practice of Gas Chromatography*, 2nd ed., Wiley Interscience, New York, 1985.
5. Poole, C.F. and Schuette, S.A., *Contemporary Practice of Chromatography*, Elsevier, Amsterdam, 1984.
6. Mann, J.R. and Preston, S.T., Selection of preferred liquid phases, *J. Chromatogr. Sci.*, 11, 216, 1973.
7. Coleman, A.E., Chemistry of liquid phases, other silicones, *J. Chromatogr. Sci.*, 11, 198, 1973.
8. Yancey, J.A., Liquid phases used in packed gas chromatographic columns. Part 1: Polysiloxane phases, *J. Chromatogr. Sci.*, 23, 161, 1985.
9. Yancey, J.A., Liquid phases used in packed gas chromatographic columns. Part 2: Use of liquid phases which are not polysiloxanes, *J. Chromatogr. Sci.*, 23, 370, 1985.
10. McReynolds, W.O., Characterization of some liquid phases, *J. Chromatogr. Sci.*, 8, 685, 1970.

### Stationary Phases for Packed Column Gas Chromatography

Compound	Suggested Stationary Phases
Alcohols C <sub>1</sub> –C <sub>5</sub>	Apiezon L, M; benzyldiphenyl; butane diol succinate (Craig polyester); carbowax 400, 600, 750, 1000, 1000 (monostearate), diethylene glycolsuccinate; di-(2-ethylexyl) sebacate; diethyl-D-tartrate; di- <i>n</i> -decyl phthalate; diglycerol; diisodecyl phthalate; dinonyl phthalate; ethylene glycol succinate; Flexol 8N8; Hallcomid M-18-OL; quadrol; Renex 678; sorbitol; tricresyl phosphate; triethanolamine
C <sub>5</sub> –C <sub>18</sub>	Butanediol succinate (Craig polyester); carbowax 1500, 1540, 4000, 4000 (dioleate), 4000 (monostearate), 6000, 20M, 20M-TPA; ethylene glycol adipate; Igepal series; Ucon series; Versamid series
Di-poly	FFAP; QF-I, Porapak-Q, Porapak-QS
Aldehydes (and ketones)	Apiezon L, M; carbowax 400, 750, 1000, 1500, 1540; di- <i>n</i> -butyl phthalate; diethylene glycol succinate; ethylene glycol succinate; Hallcomid M18; squalene; tricresyl phosphate; 1,2,3-tris (2-cyanoethoxy) propane; Ucon series
Alkaloids (includes drugs and vitamins)	Apiezon L; carbowax 20M; di-(2-ethylhexyl) sebacate; ethylene glycol adipate; ethylene glycol succinate, neopentyl glycol adipate; phenyldiethanolamine succinate; SE-30 (methyl silicone phases)
Amides	Carbowax 600 (on chromosorb T); diethylene glycol succinate; ethylene glycol succinate; neopentyl glycol sebacate; versamid 900; SE-30 (methyl silicone phases)
Amino acids (and derivatives)	Carbowax 600; diethylene glycol succinate (stabilized); Ethofat (on chromosorb T); ethylene glycol succinate; neopentyl glycol adipate; SE-30; XE-60 (methyl silicone phases)
Amines	Penwalt 213; Chromosorb 103 (see support modifiers)
Boranes	Apiezon L; beeswax; carbowax 400, 1540, 4000, 20M; castorwax; diethylene glycol succinate; di- <i>n</i> -decyl phthalate; diisodecyl phthalate; Emulphor-ON-870; ethylene glycol adipate; FFAP, polyphenyl ether (5 or 5 ring); quadrol; reoplex 400; SE-30; XE-60; sucrose acetate isobutyrate; tricresyl phosphate; Ucon series
Esters	Apiezon L; benzyldiphenyl; carbowax 20M; cyclodextrin acetate; diethylene glycol adipate; di-(2-ethylhexyl) sebacate; diisodecyl phthalate; dimer acid/OV-1 (50/50, v/v); Hallcomid M18; neopentyl glycol succinate; propylene glycol; SE-30; SE-52; XE-60; Friton X-100; Tween-80
Ethers	Apiezon L; carbowax 1500, 1540, 4000, 20M; diethylene glycol sebacate, ethylene glycol adipate
Glycols	Porapak-Q, Porapak-1S; QF-1
Halogenated compounds	Bentone 34; benzyldiphenyl; butanediol succinate (Craig polyester); carbowax 400, 1000, 4000, 20M; dibutyl phthalate; diethylene glycol succinate; di-(2-ethylhexyl) sebacate; di- <i>n</i> -decyl phthalate; dinonyl phthalate; dioctyl phthalate; β,β'-iminodipropionitrile; β,β'-oxydipropionitrile; SE-30; squalane; Tween-80
Inorganic compounds (includes organometallic compounds)	<i>n</i> -Decane; di- <i>n</i> -decyl phthalate; dimethyl sulfolane; neopentyl glycol succinate; 1,2,3-tris (2-cyanoethoxy) propane; SE-30 (methyl silicone phases)
Hydrocarbons C <sub>1</sub> –C <sub>5</sub> (aliphatic)	Carbowax 400–1500; most branched and substituted phthalate, sebacate, succinate, and adipate phases; octadecane; squalane (boiling point separations); methyl silicones
Above C <sub>5</sub> (aliphatic)	Apiezon phases; carbowax 1500, 1540, 4000, 6000, 20M; most of the high-temperature substituted adipates, phthalates, succinates, and sebacates (boiling point separations); methyl silicones
(Aromatic)	Apiezon phases; bentone-34; carbowax phases; substituted adipates, phthalates, succinates, and sebacates; tetracyanoethylated pentaerythritol; liquid crystalline phases; phenyl methyl silicone phases
Nitrogen compounds	Apiezon L; Armeen SD; butanediol succinate (Craig polyester); carbowax 400, 1500, 20M; ethylene glycol adipate; propylene glycol; tetraethylene glycol dimethylether; THEED; UCON phases
Pesticides	Carbowax 20M; diethylene glycol adipate; Epon 1001; neopentyl glycol adipate; methyl silicone phases, including gum viscosities

**Stationary Phases for Packed Column Gas Chromatography (continued)**

<b>Compound</b>	<b>Suggested Stationary Phases</b>
Phosphorous compounds	Apiezon L; carbowax 20M; di- <i>n</i> -butyl phthalate; diethylene glycol succinate; Emulphor-ON-870; ethylene glycol succinate; Reoplex-400; methyl silicone phases, including gum viscosities; squalane; STAP
Silanes	Methyl silicone phases; STAP
Sugars	Apiezon L; butanediol succinate; carbowax 4000, Hyprose SP80; mannitol; methyl silicone phases
Sulfur compounds	Apiezon L; 7,8-benzoquinoline; carbowax 1500, 20M; diethylene glycol succinate; diisodecyl phthalate; methyl silicone phases; Reoplex-400; tricresyl phosphate
Urinary and bile compounds	Ethylene glycol adipate; methyl silicone–nitrile phases

## ADSORBENTS FOR GAS–SOLID CHROMATOGRAPHY

The following table lists the more common adsorbents used in gas–solid chromatography, along with relevant information on separation and technique.<sup>1–3</sup> The adsorbents are used chiefly for the analysis of gaseous mixtures. The maximum temperatures listed represent the point of severe resolution loss. The materials are often chemically stable at much higher temperatures. The 60- to 100-mesh sizes (U.S.) are most useful for chromatographic applications. All of these materials must be activated before being used, and the degree of activation will influence the retention behavior. The user should also be aware that the adsorption of water during use will often change retention characteristics dramatically, sometimes resulting in a reversal of positions of adjacent peaks. Due to surface adsorption of solutes, some experimentation with temperature may be necessary to prevent tailing or to avoid statistical correlation (or a propagating error) among replicate analyses.<sup>4</sup>

## REFERENCES

1. Jeffery, P.G. and Kipping, P.J., *Gas Analysis by Gas Chromatography*, Pergamon Press, Oxford, 1972.
2. Cowper, C.J. and DeRose, A.J., *The Analysis of Gases by Chromatography*, Pergamon Press, Oxford, 1983.
3. Breck, D.W., *Zeolite Molecular Sieves*, John Wiley & Sons, New York, 1973.
4. Bruno, T.J., An apparatus for direct fugacity measurements on mixtures containing hydrogen, *J. Res. Natl. Bur. Stand. (U.S.)*, 90, 1127, 1985.

### Adsorbents for Gas–Solid Chromatography

Packing Name	Maximum Temperature, °C	Separation Affected	Notes
Silica gel	300	H <sub>2</sub> , air, CO, C <sub>1</sub> –C <sub>4</sub> , normal hydrocarbons, alkenes, alkynes	Used often as a second column (with a molecular sieve); very hydrophilic; requires activation; can be unpredictable; largely replaced by porous polymers
Porous silica	300	Same as silica gel	Higher surface area than silica gel; often used with a humidified carrier gas; can be coated with a conventional liquid phase; Spherosil and Porasil are examples
Alumina	300	Light hydrocarbons at ambient temperature (C <sub>1</sub> –C <sub>5</sub> ), H <sub>2</sub> , light hydrocarbons at subambient temperature	Often useful with controlled water preadsorption after activation; can be coated with a conventional liquid phase
Activated carbon	300	H <sub>2</sub> , CO, CO <sub>2</sub> , C <sub>1</sub> –C <sub>3</sub> alkanes, alkenes, alkynes	Requires oxygen-free carrier gas; largely replaced by porous polymers
Graphite	300	Light hydrocarbons, H <sub>2</sub> S, SO <sub>2</sub> , CH <sub>3</sub> SH, sour gas	Often modified with small quantities (1.5–5%) of conventional liquid phases; requires oxygen-free carrier
Carbon molecular sieve	300	H <sub>2</sub> (O <sub>2</sub> , N <sub>2</sub> co-elute), CO, CH <sub>4</sub> , H <sub>2</sub> O, CO <sub>2</sub> , C <sub>1</sub> –C <sub>3</sub> alkanes, alkenes, alkynes	High affinity for hydrocarbons; requires oxygen-free carrier
Molecular sieve, 5A	225	Air and light gas analysis; H <sub>2</sub> , O <sub>2</sub> , N <sub>2</sub> , (CH <sub>4</sub> , CO, NO, SF <sub>6</sub> co-elute)	Synthetic calcium aluminosilicate (zeolite), having an effective pore diameter of 0.5 nm, CO <sub>2</sub> is adsorbed strongly; 5A usually gives the best results of all synthetic zeolites; should be activated before use and used above critical adsorption temperature; 21.6% (mass/mass) water capacity
Molecular sieve, 13X	200	Same as 5A, but with C <sub>1</sub> –C <sub>4</sub> , alkanes, alkenes, and alkynes being separated as well	Sodium aluminosilicate (zeolite), having a larger pore size than 0.5 nm, thus producing lower retention times and less resolution; 28.6% (mass/mass) water capacity
Molecular sieve, 3A	200	Light permanent gases	Potassium aluminosilicate (zeolite) 20% (mass/mass) water capacity, smaller pore size than 0.5 nm, thus different retention characteristics
Molecular sieve, 4A	200	Light permanent gases	Sodium aluminosilicate (zeolite); 22% (mass/mass) water capacity; retention characteristics differ from 5A due to smaller pore size

## POROUS POLYMER PHASES

Porous polymer phases, first reported by Hollis,<sup>1</sup> are of great value for a wide variety of separations. They are usually white, but may darken during use, especially at higher temperatures. This darkening does not affect their performance. High-temperature conditioning is required to drive off solvent and residual monomer. The polymers may either swell or shrink with heating; thus, flow rate changes must be anticipated. The retention indices reported here are from the work of Dave.<sup>2</sup> The use of these indices is the same as for the packed column liquid phases, provided in an earlier table.

Index	Test Probe
W	Benzene
X	<i>t</i> -Butanol
Y	Methyl ethyl ketone
Z	Acetonitrile

The physical property data were taken from the work of Poole and Schuette.<sup>3</sup>

## REFERENCES

1. Hollis, O.L., Separation of gaseous mixtures using porous polyaromatic polymer beads, *Anal. Chem.*, 38, 309, 1966.
2. Dave, S., A comparison of the chromatographic properties of porous polymers, *J. Chromatogr. Sci.*, 7, 389, 1969.
3. Poole, C.F. and Schuette, S.A., *Contemporary Practice of Chromatography*, Elsevier, Amsterdam, 1984.

# Porous Polymer Phases

Packing Name	Maximum Temperature, °C	Material Type	Free-Fall Density, g/cm <sup>3</sup>	Surface Area, m <sup>2</sup> /g	Pore Diameter Average, μm	Retention Indices				Separation Affected	Notes
						W	X	Y	Z		
Chromosorb 101	275	Styrene-divinylbenzene copolymer	0.30	<50	0.3–0.4	745	565	645	580	Free fatty acids, glycols, alcohols, alkanes, esters, aldehydes, ketones, ethers	Hydrophobic; condition at 250°C; not recommended for amines or anilines; lower retention times than obtained with Chromosorb 102
Chromosorb 102	250	Styrene-divinylbenzene copolymer	0.29	300–500	0.0085	650	525	570	460	Subambient temperature: H <sub>2</sub> , O <sub>2</sub> , N <sub>2</sub> , Ar, NO, CO; ambient temperature: H <sub>2</sub> , (air + Ar + NO + CO), CH <sub>4</sub> , CO <sub>2</sub> , H <sub>2</sub> O, N <sub>2</sub> O, C <sub>2</sub> H <sub>6</sub> ; above ambient temperature: C <sub>1</sub> –C <sub>4</sub> hydrocarbons, H <sub>2</sub> S, COS, SO <sub>2</sub> , esters, ethers, alcohols, ketones, aldehydes, glycols	May entrain some species; hydrophobic; condition at 225°C; not recommended for amines or nitriles; little tailing of water or oxygenated hydrocarbons
Chromosorb 103	275	Polystyrene cross-linked	0.32	15–25	0.3–0.4	720	575	640	565	Ammonia, light amines, light amides, alcohols, aldehydes, hydrazines	Hydrophobic; high affinity for basic species; not recommended for acidic species, glycols, nitriles, nitroalkanes
Chromosorb 104	250	Acrylonitrile-divinylbenzene copolymer	0.32	100–200	0.06–0.08	845	735	860	885	Sulfur gases, ammonia, nitrogen oxides, nitriles, nitroalkanes, xylenols, water in benzene	Hydrophobic; condition at 225°C; not recommended for glycols and amines; moderately polar



**Porous Polymer Phases (continued)**

Packing Name	Maximum Temperature, °C	Material Type	Free-Fall Density, g/cm <sup>3</sup>	Surface Area, m <sup>2</sup> /g	Pore Diameter Average, μm	Retention Indices				Separation Affected	Notes
						W	X	Y	Z		
Chromosorb 105	250	Acrylic ester (polyaromatic)	0.34	600–700	0.04–0.06	635	545	580	480	Permanent and light hydrocarbon gases; aqueous solutions of light organics such as formalin	Hydrophobic; less polar than Chromosorb 104; condition at 225°C; not recommended for acidic species, glycols, amines, and amides
Chromosorb 106	250	Polystyrene cross-linked	0.28	700–800	0.05	605	505	540	405	Fatty acids from fatty alcohols, up to C <sub>5</sub> ; benzene from nonpolar organic compounds	Hydrophobic; not recommended for glycols and amines
Chromosorb 107	250	Acrylic ester cross-linked	0.30	400–500	0.8	660	620	650	550	Aqueous solutions of formaldehyde; alkynes from alkanes	Hydrophobic; moderately polar; not recommended for glycols and amines
Chromosorb 108	250	Acrylic ester cross-linked	0.30	100–200	0.25	710	645	675	605	Polar materials such as water, alcohols, aldehydes, glycols	Hydrophobic; condition at 250°C
Haysep A	165	Divinylbenzene/ethyleneglycol-dimethacrylate (high purity)	0.356	526	—					Separates permanent gases at ambient temperatures and is useful for hydrocarbons to C <sub>2</sub> , H <sub>2</sub> S, and H <sub>2</sub> O at elevated temperatures	Relatively high polarity
Haysep B	190	Divinylbenzene/polyethyleneimine	0.330	608	—					Separates C <sub>1</sub> and C <sub>2</sub> amines, and trace levels of NH <sub>3</sub> and H <sub>2</sub> O	High polarity

Haysep C	250	Divinylbenzene/ acrylonitrile	0.322	442	—	Separates polar hydrocarbons, also HCN, NH <sub>3</sub> , H <sub>2</sub> S, H <sub>2</sub>	Moderate polarity, with separation characteristics similar to Chromosorb 104
Haysep D	290	Divinylbenzene (high purity)	0.3311 (average)	795 (average)	0.0308– 0351	Separates light gases; CO, CO <sub>2</sub> , C <sub>2</sub> H <sub>2</sub> , C <sub>2</sub> hydrocarbons, H <sub>2</sub> S, H <sub>2</sub> O	Low-polarity polymer available in four formulations of different surface areas (771–802 m <sup>2</sup> /g), densities (0.3283–0.3834 g/ml), and porosities (64.2–70.4%)
Haysep N	165	Divinylbenzene/ ethyleneglycol- dimethacrylate (high purity)	0.355	405	—	Separation similar to Porapak materials; moderately high H <sub>2</sub> O retention; see retention table	Low-polarity polymer
Haysep P	250	Divinylbenzene/ styrene	0.420	165	—	Separation of low- molecular-mass materials containing halogens, sulfur, water, aldehydes, ketones, alcohols, esters, and fatty acids	Moderate to low polarity
Haysep Q	275	Divinylbenzene	0.351	582	—	Separation similar to Haysep P; see retention table	Low polarity
Haysep R	250	Divinylbenzene/ <i>N</i> -vinyl-2- pyrrolidinone	0.324	344	—	Separation similar to Haysep P; see retention table	Moderate polarity
Haysep S	250	Divinylbenzene/4- vinyl pyridine	0.334	583	—	Separation similar to Haysep P; see retention table	Moderate polarity
Haysep T	65	Ethyleneglycol- dimethacrylate (high purity)	0.381	250	—	See retention table	High polarity

**Porous Polymer Phases (continued)**

Packing Name	Maximum Temperature, °C	Material Type	Free-Fall Density, g/cm <sup>3</sup>	Surface Area, m <sup>2</sup> /g	Pore Diameter Average, μm	Retention Indices				Separation Affected	Notes
						W	X	Y	Z		
Porapak-Q	250	Ethylvinylbenzene-divinyl benzene copolymer	0.35	500–700	0.0075	630	538	580	450	Similar to Chromosorb 102	Similar to Chromosorb 102; condition at 250°C; most popular of all porous polymer phases
Porapak-P	250	Styrene-divinyl benzene copolymer	0.28	100–200	—	765	560	650	590	Similar to Porapak-Q	Hydrophobic; low polarity; larger pore size than Porapak-Q, thus lower retention times are observed; not recommended for amines or anilines; condition at 250°C
Porapak-N	200	Vinyl pyrolidone	0.39	225–350	—	735	605	705	595	Similar to Chromosorb 105; high water retention; CO <sub>2</sub> , NH <sub>3</sub> , H <sub>2</sub> O, C <sub>2</sub> H <sub>2</sub> , from light hydrocarbons	Condition at 175°C; not recommended for glycols, amines, or acidic species
Porapak-R	250	Vinyl pyrolidone	0.33	300–450	0.0076	645	545	580	455	Ethers, esters, H <sub>2</sub> O from chlorine gases (HCl, Cl <sub>2</sub> ), nitriles, nitroalkanes	Moderately polar; condition at 250°C; not recommended for glycols and amines
Porapak-S	250	Vinyl pyridine	0.35	300–450	0.0076	645	550	575	465	Normal and branched alcohols, aldehydes, ketones, halocarbons	High polarity; not recommended for acidic species and amines, condition at 250°C

Porapak-T	200	Ethylene glycol-dimethacrylate	0.44	250–300	0.009	—	675	700	635	Water in formalin (and other aqueous organic mixtures); retention characteristics similar to Chromosorb 107	Condition at 180°C; highest polarity of Porapak series; not recommended for glycols and amines
Porapak-QS	250	Ethylvinyl benzene-divinyl benzene copolymer	—	—	—	625	525	565	445	Similar to Porapak-Q at lower operating temperatures, but useful for higher-molecular-weight solutes	Silanized Porapak-Q; reduces tailing of high-polarity compounds; condition at 250°C
Porapak-PS	250	Styrene-divinyl benzene copolymer	—	—	—	—	—	—	—	Similar to Porapak-P	Silanized Porapak-P; condition at 250°C
Tenax-GC	375	<i>p</i> -2,6 Diphenyl-phenylene oxide polymer	0.37	18.6	—	—	—	—	—	Similar to Porapak-Q	Highest thermal stability of all porous polymers

<sup>a</sup> Retention indices are not available for these porous polymers, but a table of relative retentions on some representative solutes is included at the end of this section.

## RELATIVE RETENTION ON SOME HAYSEP POROUS POLYMERS

The following table provides relative retention values for Haysep polymers N, Q, R, S, and T. These data were obtained using a 2-m-long, 0.32-cm-O.D. stainless steel column, using helium as the carrier gas.

Haysep Polymer					
Compound	N	Q	R	S	T
Hydrogen	0.19	0.143	0.17	0.19	0.21
Air	0.23	0.186	0.2	0.21	0.25
Nitric oxide	0.25	0.217	0.21	0.23	0.33
Methane	0.30	0.256	0.28	0.3	0.35
Carbon dioxide	0.71	1.15	0.50	0.52	0.85
Nitrous oxide	0.80	1.43	0.59	0.59	—
Ethylene	0.83	0.74	0.78	0.78	0.9
Acetylene	1.41	0.74	1.0	0.87	2.11
Ethane	1.0	1.0	1.0	1.0	1.0
Water	10.1	1.45	0.68	4.12	19.1
Hydrogen sulfide	2.1	1.40	1.73	1.87	2.88
Hydrogen cyanide	1.93	2.31	15.6	8.26	28.8
Carbonyl sulfide	2.82	2.33	2.46	2.63	3.4
Sulfur dioxide	12.0	3.05	9.78	17.8	19.0
Propylene	4.66	3.20	3.45	3.65	4.91
Propane	4.66	3.67	3.88	4.1	4.63
Propadiene	6.50	4.12	4.39	4.7	7.55
Methylacetylene	9.5	4.12	4.84	5.14	11.3
Methyl chloride	7.43	3.93	4.67	4.92	9.2
Vinyl chloride	14.9	6.04	9.04	9.7	17.3
Ethylene oxide	17.7	6.06	8.78	9.7	23.3
Ethyl chloride	35.0	12.25	19.3	20.7	43.2
Carbon disulfide	—	32.4	—	—	40.7

## SILICONE LIQUID PHASES

The following table lists the chromatographic properties of some of the more popular polysiloxane-based liquid phases.<sup>1-8</sup> The polysiloxanes are the most widely used stationary phases in gas chromatography and are especially applicable to capillary columns. The listing provided here is far from exhaustive. Since it is impractical to present the structures of all polysiloxane-based phases, the Ohio Valley (OV) phases have been chosen as representative since their properties are among the most well characterized. The phases that are listed in the notes as similar phases have thermal and chromatographic properties similar to those of the phase described. In modern applications of capillary column gas chromatography, silicone phases are cross-linked to provide stability. Cross-linking can change the properties of a phase to some extent. The data presented here, for material that is not cross-linked, can be used as a basis for comparison.

The reader should note that there are many commercial variations of silicone liquid phases available. In compiling properties such as those listed in this table, one must strike a balance between general usefulness and simply providing information that is contained in vendor catalogs, promotional brochures, and websites. In that context, this table is meant to serve as a starting point for the design of an analysis.

The McReynolds constants are indices with respect to the following test probe compounds:

McReynolds Constant	Test Probe
1	Benzene
2	1-Butanol
3	2-Pentanone
4	1-Nitropropane
5	Pyridine
6	2-Methyl-2-pentanol
7	1-Iodobutane
8	2-Octyne
9	1,4-Dioxane
10	<i>cis</i> -Hydrindane

The use of these constants is described in the table in the section entitled “Properties of Some Liquid Phases for Packed Columns.” The viscosity data, where available, are presented in cSt, which is  $10^{-6}$  m<sup>2</sup>/sec. Cross-linked silicone phases based on the silicones are especially valuable for capillary gas chromatography. They are not specifically treated in this table since the differences in many properties are quite often subtle. The cross-linked phases have much longer lifetimes due to the effective immobilization.

### Abbreviations:

#### Solvents:

Ace—acetone

Chlor—chloroform

Tol—toluene

(When a silicone fluid is cross-linked, it will be insoluble.)

Note:  $\phi$  denotes a phenyl group in a structure.

N—nonpolar

I—intermediate polarity

P—polar

## REFERENCES

1. Yancey, J.A., Liquid phases used in packed gas chromatographic columns, *J. Chromatogr. Sci.*, 23, 161, 1985.
2. McReynolds, W.O., Characterization of some liquid-phases, *J. Chromatogr. Sci.*, 8, 685, 1970.
3. Mann, J.R. and Preston, S.T., Selection of preferred liquid-phases, *J. Chromatogr. Sci.*, 11, 216, 1973.
4. Trash, C.R., Methyl silicones: their chemistry and use as gas-chromatographic liquid-phases, *J. Chromatogr. Sci.*, 11, 196, 1973.
5. McNair, H.M. and Bonelli, E.J., *Basic Gas Chromatography*, Varian Aerograph, Palo Alto, CA, 1969.
6. Heftmann, E., *Chromatography: A Laboratory Handbook of Chromatographic and Electrophoretic Methods*, 3rd ed., Van Nostrand Reinhold, New York, 1975.
7. Grant, D.W., *Gas Liquid Chromatography*, Van Nostrand Reinhold, London, 1971.
8. Coleman, A.E., Chemistry of liquid-phases: other silicones, *J. Chromatogr. Sci.*, 11, 198, 1973.

Silicone Liquid Phases

Liquid Phase	Solvent	Average Molecular Mass	Viscosity	T <sub>min</sub> , °C	T <sub>max</sub> , °C	Polarity	McReynolds Constants										Notes
							1	2	3	4	5	6	7	8	9	10	
OV-1, dimethyl silicone (gum) <div><math display="block">\left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{---Si---O---} \\   \\ \text{CH}_3 \end{array} \right]_n</math></div>	Tol	>10 <sup>6</sup>	Gum	100	350	N	16	55	44	65	42	32	4	23	45	−1	100% methyl, low selectivity, boiling point separations; similar phases: UCC-L45, UCC-W-98, SE-30
OV-101, dimethyl silicone fluid <div><math display="block">\left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{---Si---O---} \\   \\ \text{CH}_3 \end{array} \right]_n</math></div>	Tol	3 × 10 <sup>4</sup>	1500	20	350	N	17	57	45	67	43	33	4	23	46	−2	100% methyl, low selectivity, boiling point separations; similar phases: DC-11, DC-200, DC-550, SF-96, SP-2100, STAP
OV-3, phenylmethyl-dimethyl silicone <div><math display="block">\left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{---Si---O---} \\   \\ \text{CH}_3 \end{array} \right]_n \left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{---Si---O---} \\   \\ \phi \end{array} \right]_m</math></div>	Ace	2 × 10 <sup>4</sup>	500	20	350	I	44	86	81	124	88	55	39	46	84	17	10% phenylmethyl; similar to SE-52
OV-7, phenylmethyl-dimethyl silicone <div><math display="block">\left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{---Si---O---} \\   \\ \text{CH}_3 \end{array} \right]_n \left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{---Si---O---} \\   \\ \phi \end{array} \right]_m</math></div>	Ace	1 × 10 <sup>4</sup>	500	20	350	I	69	113	111	171	128	77	68	66	120	35	20% phenylmethyl
OV-11, phenylmethyl-dimethyl silicone <div><math display="block">\left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{---Si---O---} \\   \\ \text{CH}_3 \end{array} \right]_n \left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{---Si---O---} \\   \\ \phi \end{array} \right]_m</math></div>	Ace	7 × 10 <sup>3</sup>	500	0	350	I	102	142	145	219	178	100	103	92	164	59	35% phenylmethyl; similar phase: DC-710



Silicone Liquid Phases (continued)

Liquid Phase	Solvent	Average Molecular Mass	Viscosity	T <sub>min</sub> , °C	T <sub>max</sub> , °C	Polarity	McReynolds Constants										Notes
							1	2	3	4	5	6	7	8	9	10	
OV-17, phenylmethyl silicone <div><math display="block">\left[ \begin{array}{c} \text{CH}_3 \\   \\ -\text{Si}-\text{O}- \\   \\ \phi \end{array} \right]_n</math></div>	Ace	4 × 10 <sup>3</sup>	1300	20	350	I	119	158	162	243	202	112	119	105	184	69	50% methyl, similar phase: SP-2250
OV-22, phenylmethyl-dimethyl silicone <div><math display="block">\left[ \begin{array}{c} \text{CH}_3 \\   \\ -\text{Si}-\text{O}- \\   \\ \phi \end{array} \right]_n \left[ \begin{array}{c} \phi \\   \\ -\text{Si}-\text{O}- \\   \\ \phi \end{array} \right]_m</math></div>	Ace	8 × 10 <sup>3</sup>	>50,000	20	350	I	160	188	191	283	253	133	152	132	228	99	65% phenyl
OV-25, phenylmethyl-dimethyl silicone <div><math display="block">\left[ \begin{array}{c} \text{CH}_3 \\   \\ -\text{Si}-\text{O}- \\   \\ \phi \end{array} \right]_n \left[ \begin{array}{c} \phi \\   \\ -\text{Si}-\text{O}- \\   \\ \phi \end{array} \right]_m</math></div>	Ace	1 × 10 <sup>4</sup>	100,000	20	350	I	178	204	208	305	280	144	169	147	215	113	75% phenyl
OV-61, diphenyl-dimethyl silicone <div><math display="block">\left[ \begin{array}{c} \phi \\   \\ -\text{Si}-\text{O}- \\   \\ \phi \end{array} \right]_n \left[ \begin{array}{c} \text{CH}_3 \\   \\ -\text{Si}-\text{O}- \\   \\ \text{CH}_3 \end{array} \right]_m</math></div>	Tol	4 × 10 <sup>4</sup>	>50,000	20	350	I	101	143	142	213	174	99	—	86	—	—	33% phenyl

OV-73, diphenyl-dimethyl silicone gum	Tol	$8 \times 10^5$	Gum	20	350	I	40	86	76	114	85	57	—	39	—	—	5.5% phenyl, similar phases: SE-52, SE- 54
$\left[ \begin{array}{c} \phi \\   \\ -\text{Si}-\text{O}- \\   \\ \phi \end{array} \right]_n \left[ \begin{array}{c} \text{CH}_3 \\   \\ -\text{Si}-\text{O}- \\   \\ \text{CH}_3 \end{array} \right]_m$																	
OV-105, cyano propylmethyl-dimethyl silicone	Ace		1500	20	250	N, I	36	108	93	139	86	74	—	29	—	—	
$\left[ \begin{array}{c} \text{CH}_3 \\   \\ -\text{Si}-\text{O}- \\   \\ (\text{CH}_2)_2 \\   \\ \text{C}\equiv\text{N} \end{array} \right]_n \left[ \begin{array}{c} \text{CH}_3 \\   \\ -\text{Si}-\text{O}- \\   \\ \text{CH}_3 \end{array} \right]_m$																	
OV-202, trifluoropropyl-methyl silicone	Chlor	$1 \times 10^4$	500	0	275	I, P	146	238	358	468	310	202	139	56	283	60	50% trifluoropropyl fluid, similar phase: SP-2401
$\left[ \begin{array}{c} \text{CH}_3 \\   \\ -\text{Si}-\text{O}- \\   \\ (\text{CH}_2)_2 \\   \\ \text{CF}_3 \end{array} \right]_n$																	
OV-210, trifluoropropyl-methyl silicone	Chlor	$2 \times 10^5$	10,000	20	275	I, P	146	238	358	468	310	206	139	56	283	60	50% trifluoropropyl, similar phases: QF-1, FS-1265, SD-2401
$\left[ \begin{array}{c} \text{CH}_3 \\   \\ -\text{Si}-\text{O}- \\   \\ (\text{CH}_2)_2 \\   \\ \text{CF}_3 \end{array} \right]_n$																	

# Silicone Liquid Phases (continued)

Liquid Phase	Solvent	Average Molecular Mass	Viscosity	T <sub>min</sub> <sup>a</sup> °C	T <sub>max</sub> <sup>a</sup> °C	Polarity	McReynolds Constants										Notes
							1	2	3	4	5	6	7	8	9	10	
OV-215, trifluoropropyl-methyl silicone gum			Gum			I, P	149	240	363	478	315	208	—	56	—	—	50% trifluoropropyl
<div><div><div><div><div></div><div>CH<sub>3</sub></div></div><div><div><div><div></div><div>—Si—O—</div><div>(CH<sub>2</sub>)<sub>2</sub></div><div>CF<sub>3</sub></div></div></div></div></div></div><div><div><div><div></div><div>CH<sub>3</sub></div></div><div><div><div><div></div><div>—Si—O—</div><div>(CH<sub>2</sub>)<sub>2</sub></div><div>C≡N</div></div></div></div></div></div><div><div><div><div></div><div>CH<sub>3</sub></div></div><div><div><div><div></div><div>—Si—O—</div><div>φ</div></div></div></div></div></div></div>																	
OV-225, cyanopropyl- methylphenyl methylsilicone	Ace	8 × 10 <sup>3</sup>	9000	20	275	I, P	228	369	338	492	386	282	226	150	342	117	25% phenyl, 25% cyanopropylmethyl; similar phases: EX- 60, AN-600
<div><div><div><div><div></div><div>CH<sub>3</sub></div></div><div><div><div><div></div><div>—Si—O—</div><div>(CH<sub>2</sub>)<sub>2</sub></div><div>C≡N</div></div></div></div></div></div><div><div><div><div></div><div>CH<sub>3</sub></div></div><div><div><div><div></div><div>—Si—O—</div><div>φ</div></div></div></div></div></div></div>																	
OV-275, dicyanoallyl silicone	Ace	5 × 10 <sup>3</sup>	20,000	20	275	P	781	1006	885	1177	1089	—	—	—	—	—	Carborane-methyl silicone; siloxane to carborane ratio, 4:1; used for methyl esters, aromatic amines, halogenated alcohols, pesticides, polyphenyl ethers, silicone oils
Dexsil 300 copolymer	Chlor	16,000– 20,000	Waxy solid	50	450	I	47	80	103	148	96	—	—	—	—	—	
<div><div><div><div><div></div><div>CH<sub>3</sub>—O—CH<sub>3</sub></div></div><div><div><div><div></div><div>CH<sub>3</sub>—Si—CH<sub>3</sub></div><div>[B]—Si—O—Si—O—Si—O—</div><div>CH<sub>3</sub>CH<sub>3</sub>CH<sub>3</sub></div></div></div></div></div></div><div><div><div><div></div><div>CH<sub>3</sub></div></div><div><div><div><div></div><div>CH<sub>3</sub></div></div><div><div><div><div></div><div>φ</div></div></div></div></div></div></div></div></div>																	
<div>[B] = CB<sub>10</sub>H<sub>10</sub>C, meta-carborane</div>																	

Dexsil 400	Chlor	12,000–16,000	—	20	375	I	60	115	140	188	174	—	—	—	—	—	Carborane-methyl phenyl silicone copolymer; siloxane to carborane ratio, 5:1
$  \left[ \begin{array}{c}  \text{CH}_3 - \text{Si} - \text{CH}_3 \\    \\  [\text{B}] - \text{Si} - \text{O} - \text{Si} - \text{O} - \text{Si} - \text{O} - \\    \quad   \quad   \quad   \\  \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3  \end{array} \right]_n  $ <p>[B] = CB<sub>10</sub>H<sub>10</sub>C meta-carborane</p>																	
Dexsil 410	Chlor	9000–12,000		20	375	I	85	165	170	240	180	—	—	—	—	—	Carborane-methyl- β-silicone cyanoethyl copolymer; siloxane to carborane ratio, 5:1
$  \left[ \begin{array}{c}  \text{CH}_3 - \text{Si} - \text{CH}_3 \\    \\  \text{O} \\    \\  \text{CH}_3 - \text{Si} - \text{CH}_3 \\    \quad   \quad   \quad   \\  [\text{B}] - \text{Si} - \text{O} - \text{Si} - \text{O} - \text{Si} - \text{O} - \\    \quad   \quad   \quad   \\  \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3  \end{array} \right]_n  $ <p>[B] = CB<sub>10</sub>H<sub>10</sub>C</p>																	

## MESOGENIC STATIONARY PHASES

The following table lists the liquid crystalline materials that are useful as gas chromatographic stationary phases in both packed and open tubular column applications. In each case, the name, structure, and transition temperatures are provided (where available), along with a description of the separations that have been done using these materials. The table has been divided into two sections. The first section contains information on phases that have either smectic or nematic phases or both, while the second section contains mesogens that have a cholesteric phase. It should be noted that each material may be used for separations other than those listed, but the listing contains the applications reported in the literature.

It should be noted that some of the mesogens listed in this table are not commercially available and must be prepared synthetically for laboratory use. The reader is referred to the appropriate citation for details.

## REFERENCES

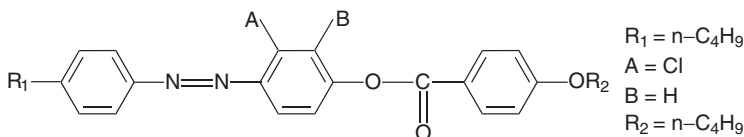
1. Panse, D.G., Naikwadi, K.P., Bapat, B.V., and Ghatge, B.B., Applications of laterally mono and disubstituted liquid crystals as stationary phases in gas liquid chromatography, *Ind. J. Technol.*, 19, 518, 1981.
2. Grushka, E. and Solsky, J.F., p-Azoxyanisole liquid crystal as a stationary phase for capillary column gas chromatography, *Anal. Chem.*, 45, 1836, 1973.
3. Witkiewicz, Z. and Stanislaw, P., Separation of close-boiling compounds on liquid-crystalline stationary phases, *J. Chromatogr.*, 154, 60, 1978.
4. Naikwadi, K.P., Panse, D.G., Bapat, B.V., and Ghatge, B.B., I. Synthesis and application of stationary phases in gas-liquid chromatography, *J. Chromatogr.*, 195, 309, 1980.
5. Dewar, M. and Schroeder, J.P., Liquid crystals as solvents. I. The use of nematic and smectic phases in gas-liquid chromatography, *J. Am. Chem. Soc.*, 86, 5235, 1964.
6. Dewar, M., Schroeder, J.P., and Schroeder, D., Molecular order in the nematic mesophase of 4,4'-di-n-hexyloxyazoxybenzene and its mixture with 4,4'-dimethoxyazoxybenzene, *J. Org. Chem.*, 32, 1692, 1967.
7. Naikwadi, K.P., Rokushika, S., and Hatano, H., New liquid crystalline stationary phases for gas chromatography of positional and geometrical isomers having similar volatilities, *J. Chromatogr.*, 331, 69, 1985.
8. Richmond, A.B., Use of liquid crystals for the separation of position isomers of disubstituted benzenes, *J. Chromatogr. Sci.*, 9, 571, 1971.
9. Witkiewicz, Z., Pietrzyk, M., and Dabrowski, R., Structure of liquid crystal molecules and properties of liquid-crystalline stationary phases in gas chromatography, *J. Chromatogr.*, 177, 189, 1979.
10. Ciosek, M., Witkiewicz, Z., and Dabrowski, R., Direct gas: chromatographic determination of 2-naphthylamine in 1-naphthylamine on liquid-crystalline stationary phases, *Chemia Analityczna*, 25, 567, 1980.
11. Jones, B.A., Bradshaw, J.S., Nishioka, M., and Lee, M.L., Synthesis of smectic liquid-crystalline polysiloxanes from biphenylcarboxylate esters and their use as stationary phases for high-resolution gas chromatography, *J. Org. Chem.*, 49, 4947, 1984.
12. Porcaro, P.J. and Shubiak, P., Liquid crystals as substrates in the GLC of aroma chemicals, *J. Chromatogr. Sci.*, 9, 689, 1971.
13. Witkiewicz, Z., Suprynowicz, Z., Wojcik, J., and Dabrowski, R., Separation of the isomers of some disubstituted benzenes on liquid crystalline stationary phases in small-bore packed micro-columns, *J. Chromatogr.*, 152, 323, 1978.
14. Dewar, M. and Schroeder, J.P., Liquid-crystals as solvents. II. Further studies of liquid crystals as stationary phases in gas-liquid chromatography, *J. Org. Chem.*, 30, 3485, 1965.
15. Witkiewicz, Z., Szule, J., Dabrowski, R., and Sadowski, J., Properties of liquid crystalline cyanoazoxybenzene alkyl carbonates as stationary phases in gas chromatography, *J. Chromatogr.*, 200, 65, 1980.

16. Witkiewicz, Z., Suprynowicz, Z., and Dabrowski, R., Liquid crystalline cyanoazoxybenzene alkyl carbonates as stationary phases in small-bore packed micro-columns, *J. Chromatogr.*, 175, 37, 1979.
17. Lochmüller, C.H. and Souter, R.W., Direct gas chromatographic resolution of enantiomers on optically active mesophases, *J. Chromatogr.*, 88, 41, 1974.
18. Markides, K.E., Nishioka, M., Tarbet, B.J., Bradshaw, J.S., and Lee, M.L., Smectic biphenylcarboxylate ester liquid crystalline polysiloxane stationary phase for capillary gas chromatography, *Anal. Chem.*, 57, 1296, 1985.
19. Vetrova, Z.P., Karabanov, N.T., Shuvalova, T.N., Ivanova, L.A., and Yashin, Y.I., The use of p-n-butyl oxybenzoic acid as liquid crystalline sorbent in gas chromatography, *Chromatographia*, 20, 41, 1985.
20. Cook, L.E. and Spangelo, R.C., Separation of monosubstituted phenol isomers using liquid crystals, *Anal. Chem.*, 46, 122, 1974.
21. Kong, R.C. and Milton, L.L., Mesogenic polysiloxane stationary phase for high resolution gas chromatography of isomeric polycyclic aromatic compounds, *Anal. Chem.*, 54, 1802, 1982.
22. Bartle, K.D., El-Nasri, A.I., and Frere, B., *Identification and Analysis of Organic Pollutants in Air*, Ann Arbor Science, Ann Arbor, MI, 1984, 183 pp.
23. Finkleman, H., Laub, R.J., Roberts, W.E., and Smith, C.A., Use of mixed phases for enhanced gas chromatographic separation of polycyclic aromatic hydrocarbons. II. Phase transition behavior, mass-transfer non-equilibrium, and analytical properties of a mesogen polymer solvent with silicone diluents, in *Polynuclear Aromatic Hydrocarbons*, Phys. Biol. Chem. 6th Int. Symp., Cooke, M., Ed., Battelle Press, Columbus, OH, 1982, p. 275.
24. Janini, G.M., Recent usage of liquid crystal stationary phases in gas chromatography, *Adv. Chromatogr.*, 17, 231, 1979.
25. Witkiewicz, Z. and Waclawczyk, A., Some properties of high-temperature liquid crystalline stationary phases, *J. Chromatogr.*, 173, 43, 1979.
26. Zielinski, W.L., Johnston, R., and Muschik, G.M., Nematic liquid crystal for gas-liquid chromatographic separation of steroid epimers, *Anal. Chem.*, 48, 907, 1976.
27. Smith, T.R. and Wozny, M.E., Gas chromatographic separation of underivatized steroids using BPhBT liquid crystal stationary phase, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 3, 333, 1980.
28. Barrall, E.M., Porter, R.S., and Johnson, J.F., Gas chromatography using cholesteryl ester liquid phase, *J. Chromatogr.*, 21, 392, 1966.
29. Heath, R.R. and Dolittle, R.E., Derivatives of cholesterol cinnamate: a comparison of the separations of geometrical isomers when used as gas chromatographic stationary phases, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 6, 16, 1983.
30. Sonnet, P.E. and Heath, R.R., Aryl substituted diastereomeric alkenes: gas chromatographic behavior on a non-polar versus a liquid crystal phase, *J. Chromatogr.*, 321, 127, 1985.

## Mesogenic Stationary Phases

**Name:** 2-Chloro-4'-*n*-butyl-4-(4-*n*-butoxybenzoyloxy) azobenzene

**Structure:**



**Thermophysical Properties:**

Solid → nematic 87.2°C

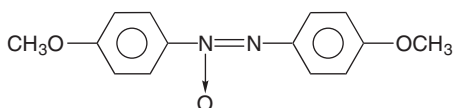
Nematic → isotropic 168°C

**Analytical Properties:** Separation of close-boiling disubstituted benzenes

**Reference:** 1

**Name:** *p*-Azoxyanisole (4,4'-dimethoxyazoxybenzene)

**Structure:**



**Thermophysical Properties:**

Solid → nematic 118°C

Nematic → isotropic 135°C

*Note:* Supercooling has been noted at 110°C by observing nematic-like properties; liquid crystalline behavior can sometimes persist to 102°C

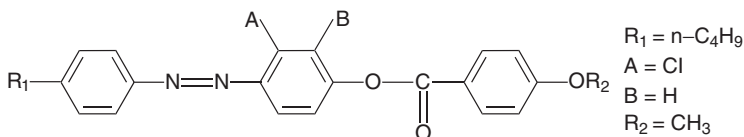
**Analytical Properties:**

Separation of xylenes; separation of lower-molecular-weight aromatic hydrocarbon isomers, especially at the lower area of the nematic region.

**Reference:** 2

**Name:** 2-Chloro-4'-*n*-butyl-4-(4-*n*-butoxybenzoyloxy) azobenzene

**Structure:**



**Thermophysical Properties:**

Solid → nematic 92.5°C

Nematic → isotropic 176°C

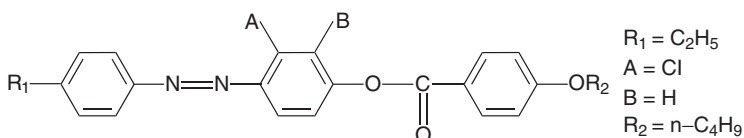
*Note:* Supercooling has been noted at 110°C by observing nematic-like properties; liquid crystalline behavior can sometimes persist to 102°C

**Analytical Properties:** Separation of close-boiling disubstituted benzenes

**Reference:** 1

**Name:** 2-Chloro-4'-*n*-butyl-4-(4-*n*-butoxybenzoyloxy) azobenzene

**Structure:**



## Mesogenic Stationary Phases (continued)

### Thermophysical Properties:

Solid → nematic 117°C  
Nematic → isotropic 172°C

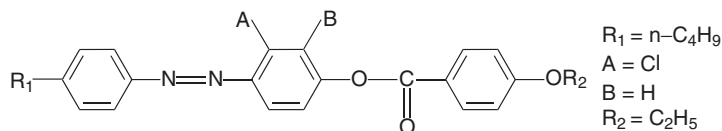
*Note:* Supercooling has been noted at 110°C by observing nematic-like properties; liquid crystalline behavior can sometimes persist to 102°C

**Analytical Properties:** Separation of close-boiling disubstituted benzenes

**Reference:** 1

**Name:** 2-Chloro-4'-*n*-butyl-4-(4-ethoxybenzoyloxy) azobenzene

**Structure:**



### Thermophysical Properties:

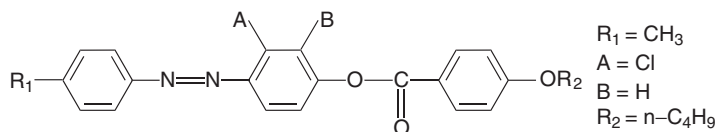
Solid → nematic 89.7°C  
Nematic → isotropic 170°C

**Analytical Properties:** Separation of close-boiling disubstituted benzenes

**Reference:** 1

**Name:** 2-Chloro-4'-methyl-4-(4-butoxybenzoyloxy) azobenzene

**Structure:**



### Thermophysical Properties:

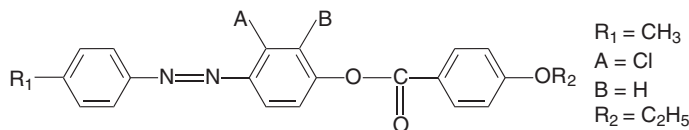
Solid → nematic 112°C  
Nematic → isotropic 165°C

**Analytical Properties:** Separation of close-boiling disubstituted benzenes

**Reference:** 1

**Name:** 2-Chloro-4'-*n*-methyl-4-(4-ethoxybenzoyloxy) azobenzene

**Structure:**



### Thermophysical Properties:

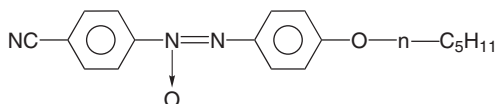
Solid → nematic 128.3°C  
Nematic → isotropic 185°C

**Analytical Properties:** Separation of close-boiling disubstituted benzenes

**Reference:** 1

**Name:** *p*-Cyano-*p*'-pentoxyazoxybenzene

**Structure:**





## Mesogenic Stationary Phases (continued)

### Thermophysical Properties:

Solid → nematic 124°C

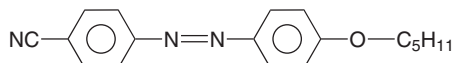
Nematic → isotropic 153°C

**Analytical Properties:** Complete separation of ethyltoluenes, chlorotoluenes, bromotoluenes, and dichlorobenzenes; also, ethylbenzene from xylenes and propylbenzene from ethyltoluenes

**Reference:** 3

**Name:** *p*-Cyano-*p*'-pentoxyazobenzene

**Structure:**



### Thermophysical Properties:

Solid → nematic 106°C

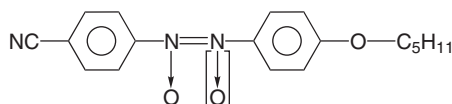
Nematic → isotropic 116°C

**Analytical Properties:** Separation of ethyltoluenes, chlorotoluenes, bromotoluenes, and dichlorobenzenes; also, ethylbenzenes from xylenes and propylbenzenes from ethylbenzenes

**Reference:** 3

**Name:** *p*-Cyano-*p*'-pentoxyazoxybenzene (mixed isomers)

**Structure:**



### Thermophysical Properties:

Solid → nematic 93.5°C

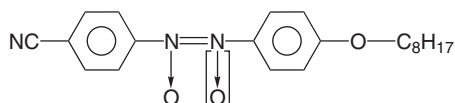
Nematic → isotropic 146.5°C

**Analytical Properties:** Complete separation of ethyltoluenes, chlorotoluenes, bromotoluenes, and dichlorobenzenes; also, ethylbenzene from xylenes and propylbenzene from ethyltoluenes

**Reference:** 3

**Name:** *p*-Cyano-*p*'-octoxyazoxybenzene (mixed isomers)

**Structure:**



### Thermophysical Properties:

Solid → smectic 71°C

Smectic → nematic 117°C

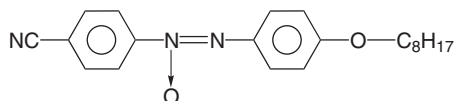
Nematic → isotropic 135°C

**Analytical Properties:** Separation of ethyltoluenes, chlorotoluenes, bromotoluenes, and dichlorobenzenes; also, ethylbenzene from xylenes and propylbenzene from ethylbenzenes

**Reference:** 3

**Name:** *p*-Cyano-*p*'-octoxyazoxybenzene

**Structure:**



## Mesogenic Stationary Phases (continued)

### Thermophysical Properties:

Solid → smectic 100.5°C

Smectic → nematic 138.5°C

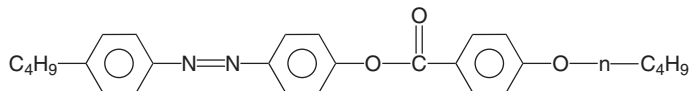
Nematic → isotropic 148.5°C

**Analytical Properties:** Separation of ethyltoluenes, chlorotoluenes, bromotoluenes, and dichlorobenzenes; also, ethylbenzene from xylenes and propylbenzene from ethylbenzenes

**Reference:** 3

**Name:** 4'-*n*-Butyl-4-(4-*n*-butoxybenzoyloxy) azobenzene

**Structure:**



### Thermophysical Properties:

Solid → nematic 94°C

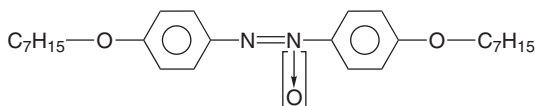
Nematic → isotropic 234.5°C

**Analytical Properties:** Separation of chlorinated biphenyls

**Reference:** 4

**Name:** 4,4'-Di-*n*-heptyloxyazoxybenzene

**Structure:**



### Thermophysical Properties:

Solid → nematic 95°C

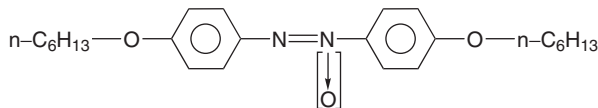
Nematic → isotropic 127°C

**Analytical Properties:** Separation of *meta*- and *para*-xylene in nematic region

**Reference:** 5

**Name:** 4,4'-Di-*n*-hexyloxyazoxybenzene

**Structure:**



### Thermophysical Properties:

Solid → nematic 81°C

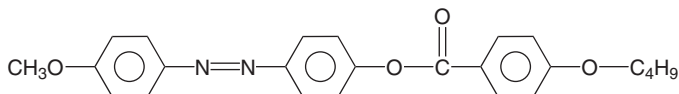
Nematic → isotropic 129°C

**Analytical Properties:** Separation of *meta*- and *para*-xylene using gas chromatography

**Reference:** 5, 6

**Name:** 4'-Methoxy-4-(4-*n*-butoxybenzoyloxy) azobenzene

**Structure:**



## Mesogenic Stationary Phases (continued)

### Thermophysical Properties:

Solid → nematic 116°C

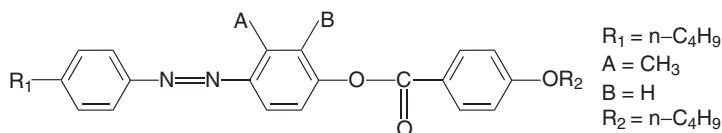
Nematic → isotropic 280°C

**Analytical Properties:** Separation of chlorinated biphenyls

**Reference:** 4

**Name:** 2-Methyl-4'-*n*-butyl-4-(4-*n*-butoxybenzoyloxy) azobenzene

**Structure:**



### Thermophysical Properties:

Solid → nematic 90°C

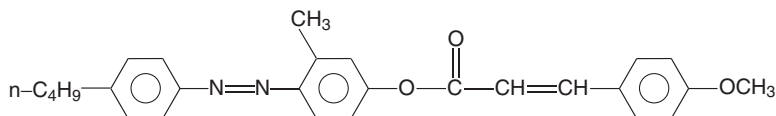
Nematic → isotropic 175°C

**Analytical Properties:** Separation of close-boiling disubstituted benzenes

**Reference:** 1

**Name:** 2-Methyl-4'-*n*-butyl-4-(*p*-methoxycinnamoyloxy) azobenzene

**Structure:**



### Thermophysical Properties:

Solid → nematic 109°C

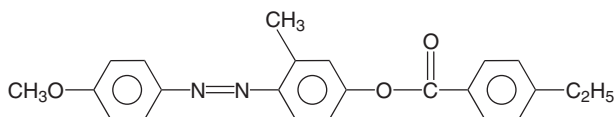
Nematic → isotropic 253°C

**Analytical Properties:** Separation of positional isomers of aromatic hydrocarbons

**Reference:** 7

**Name:** 2-Methyl-4'-methoxy-4-(4-ethoxybenzoyloxy) azobenzene

**Structure:**



### Thermophysical Properties:

Solid → nematic 125°C

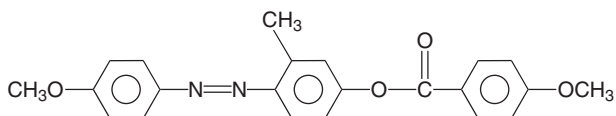
Nematic → isotropic 244°C

**Analytical Properties:** Separation of chlorinated biphenyls

**Reference:** 4

**Name:** 2-Methyl-4'-methoxy-4-(4-methoxybenzoyloxy) azobenzene

**Structure:**



## Mesogenic Stationary Phases (continued)

### Thermophysical Properties:

Solid → nematic 160°C

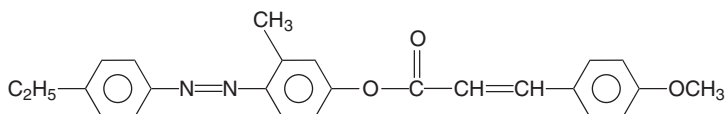
Nematic → isotropic 253°C

**Analytical Properties:** Separation of chlorinated biphenyls

**Reference:** 4

**Name:** 2-Methyl-4'-ethyl-4-(4'-methoxycinnamyloxy) azobenzene

**Structure:**



### Thermophysical Properties:

Solid → nematic 126°C

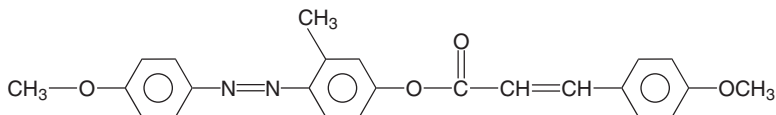
Nematic → isotropic 262°C

**Analytical Properties:** Separation of polyaromatic hydrocarbons and insect sex pheromones

**Reference:** 5

**Name:** 2-Methyl-4'-methoxy-4-(p-methoxycinnamoyloxy) azobenzene

**Structure:**



### Thermophysical Properties:

Solid → nematic 149°C

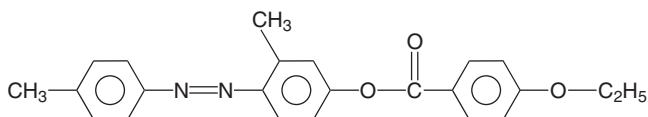
Nematic → isotropic 298°C

**Analytical Properties:** Separation of positional isomers of aromatic compounds and geometrical isomers of sex pheromones

**Reference:** 7

**Name:** 2-Methyl-4'-methyl-4-(4-ethoxybenzoyloxy) azobenzene

**Structure:**



### Thermophysical Properties:

Solid → nematic 125°C

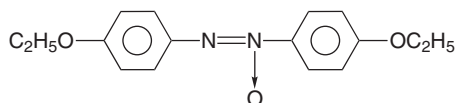
Nematic → isotropic 220°C

**Analytical Properties:** Separation of chlorinated biphenyls

**Reference:** 4

**Name:** 4,4'-Azoxyphenetole

**Structure:**



## Mesogenic Stationary Phases (continued)

### Thermophysical Properties:

Solid → nematic 138°C

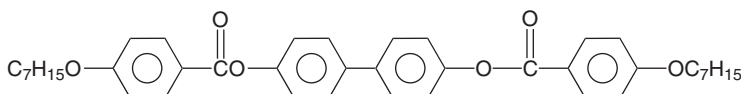
Nematic → isotropic 168°C

**Analytical Properties:** Separation of *meta*- and *para*-isomers of disubstituted benzenes

**Reference:** 8

**Name:** 4,4-Biphenylene-bis-[*p*-(heptoxy) benzoate]

**Structure:**



### Thermophysical Properties:

Solid → smectic 150°C

Smectic → nematic 211°C

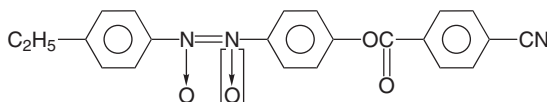
Nematic → isotropic 316°C

**Analytical Properties:** Separation of *meta*- and *para*-isomers of disubstituted benzenes

**Reference:** 8

**Name:** *p*'-Ethylazoxybenzene *p*-cyanobenzoate (mixed isomers)

**Structure:**



### Thermophysical Properties:

Melting range → 114–136°C

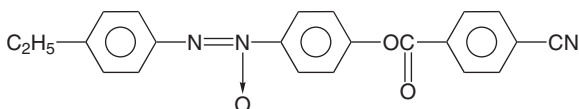
Nematic → isotropic >306°C

**Analytical Properties:** Separation of substituted xylenes

**Reference:** 9

**Name:** *p*'-Ethylazoxybenzene *p*-cyanobenzoate (pure isomer)

**Structure:**



### Thermophysical Properties:

Solid → nematic 115°C

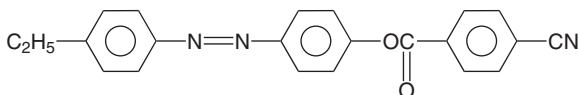
Nematic → isotropic 294°C

**Analytical Properties:** Separation of nitronaphthalenes

**Reference:** 10

**Name:** *p*'-Ethylazobenzene *p*-cyanobenzoate

**Structure:**



### Thermophysical Properties:

Solid → nematic 138–140°C

Nematic → isotropic 292°C

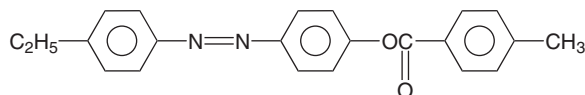
**Analytical Properties:** Separation of substituted xylenes

**Reference:** 9

### Mesogenic Stationary Phases (continued)

**Name:** *p*-Ethylazobenzene *p*-methylbenzoate

**Structure:**



**Thermophysical Properties:**

Solid → nematic 108°C

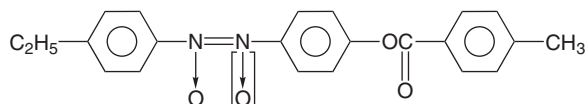
Nematic → isotropic 230°C

**Analytical Properties:** Separation of nitronaphthalenes

**Reference:** 10

**Name:** *p*-Ethylazoxybenzene *p*-methylbenzoate (mixed isomers)

**Structure:**



**Thermophysical Properties:**

(directly after crystallization)

Crystal → nematic 97.5°C

Nematic → isotropic 250.5°C

(after melting and cooling)

Crystal → nematic 87.5–97.5°C

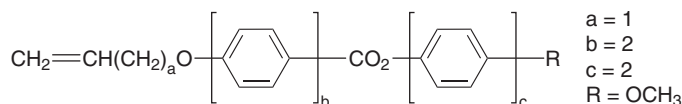
Nematic → isotropic 250.5°C

**Analytical Properties:** Separation of substituted xylenes

**Reference:** 9

**Name:** 4'-Methoxybiphenyl-4,4'-[(allyloxy)phenyl] benzoate

**Structure:**



**Thermophysical Properties:**

Solid → nematic 214°C

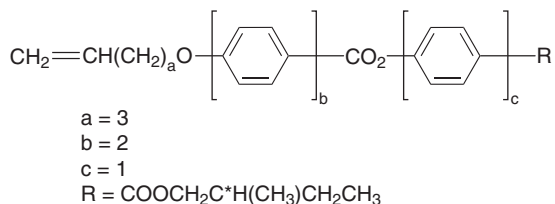
Nematic → isotropic 290°C

**Analytical Properties:** Suggested for separation of polycyclic aromatic compounds

**Reference:** 11

**Name:** (S)-4-[(2-Methyl-1-butoxy)carbonyl]phenyl-4-[4-(4-pentenloxy)phenyl] benzoate

**Structure:**



**Thermophysical Properties:**

Solid → smectic 105°C

Smectic → isotropic 198°C

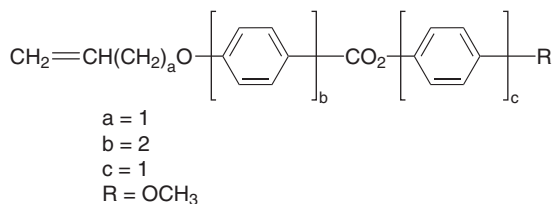
**Analytical Properties:** Suggested for separation of polycyclic aromatic compounds

**Reference:** 11

### Mesogenic Stationary Phases (continued)

**Name:** 4-Methoxyphenyl-4-[4-(allyloxy) phenyl] benzoate

**Structure:**



**Thermophysical Properties:**

Solid → nematic 137°C

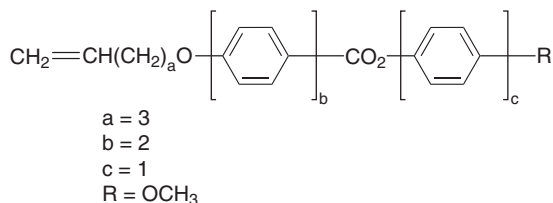
Nematic → isotropic 243°C

**Analytical Properties:** Suggested for the separation of polycyclic aromatic compounds

**Reference:** 11

**Name:** 4-Methoxyphenyl-4-[4-(4-pentenylloxy) phenyl] benzoate

**Structure:**



**Thermophysical Properties:**

Solid → smectic 133°C

Smectic → nematic 172°C

Nematic → isotropic 253°C

**Analytical Properties:** Suggested for separation of polycyclic aromatic compounds

**Reference:** 11

**Name:** *p*-Phenylene-*bis*-4-*n*-heptyloxybenzoate

**Structure:**



**Thermophysical Properties:**

Solid → smectic 83°C

Smectic → nematic 125°C

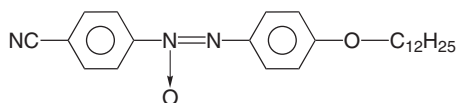
Nematic → isotropic 204°C

**Analytical Properties:** Separation of 1- and 2-ethylnaphthalene; baseline separation of pyrazines

**Reference:** 12

**Name:** 4-[(4-Dodecyloxyphenyl)azoxy]-benzonitrile

**Structure:**



## Mesogenic Stationary Phases (continued)

### Thermophysical Properties:

Solid → smectic 106°C

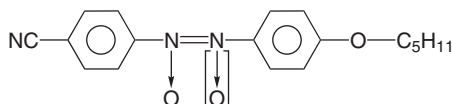
Smectic → isotropic 147°C

**Analytical Properties:** Marginal effectiveness in separating disubstituted benzene isomers

**Reference:** 13

**Name:** 4-[(4-Pentyloxyphenyl)azoxy]-benzonitrile (mixed isomers)

**Structure:**



### Thermophysical Properties:

Solid → nematic 94°C

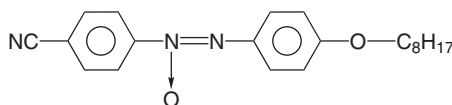
Nematic → isotropic 141.5°C

**Analytical Properties:** Does not separate diethylbenzene (DEB) isomers; good separation of disubstituted benzene isomers

**Reference:** 13

**Name:** 4-[(4-Octyloxyphenyl)azoxy]-benzonitrile

**Structure:**



### Thermophysical Properties:

Solid → smectic 101.5°C

Smectic → nematic 137°C

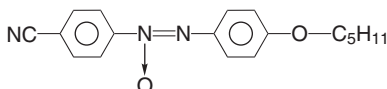
Nematic → isotropic 151.5°C

**Analytical Properties:** Separates diethylbenzene isomers

**Reference:** 13

**Name:** 4-[(4-Pentyloxyphenyl)azoxy]-benzonitrile

**Structure:**



### Thermophysical Properties:

Solid → nematic 124°C

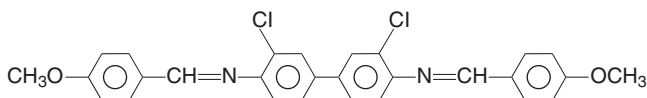
Nematic → isotropic 153°C

**Analytical Properties:** Complete separation of dichlorobenzene or bromotoluene isomers at 126°C; complete separation of chlorotoluene isomers at 87°C; partial separation of *m*- and *p*-xylenes at 87°C

**Reference:** 13

**Name:** 4,4'-Bis-(*p*-methoxybenzylidene amino)-3,3'-dichloro biphenyl

**Structure:**





## Mesogenic Stationary Phases (continued)

### Thermophysical Properties:

Solid → nematic 154°C

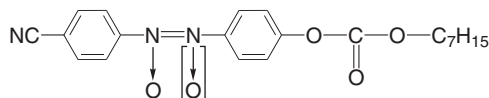
Nematic → isotropic 344°C

**Analytical Properties:** Separation of dimethylbenzene isomers, dihalobenzene isomers (Cl, Br), haloketone benzene isomers, dimethoxybenzene isomers

**Reference:** 14

**Name:** Azoxybenzene *p*-cyano-*p*'-heptyl carbonate

**Structure:**



### Thermophysical Properties:

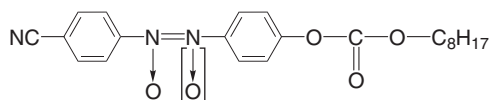
Solid → nematic 66°C

**Analytical Properties:** Separation of disubstituted benzene isomers

**Reference:** 15

**Name:** Azoxybenzene *p*-cyano-*p*'-octyl carbonate (mixed isomers)

**Structure:**



### Thermophysical Properties:

Solid → smectic 60.5°C

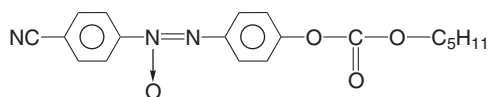
Smectic → nematic 119.5°C

**Analytical Properties:** Separation of ethyltoluenes, chlorotoluenes, bromotoluenes, dichlorobenzenes; also, ethylbenzenes from xylenes and propylbenzenes from ethylbenzenes

**Reference:** 15

**Name:** Azoxybenzene *p*-cyano-*p*'-pentyl carbonate (pure isomer)

**Structure:**



### Thermophysical Properties:

Solid → nematic 60.5°C

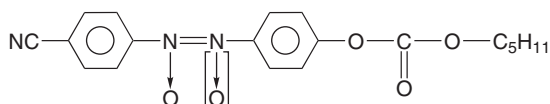
Nematic → isotropic 132°C

**Analytical Properties:** Separation of ethyltoluenes, chlorotoluenes, bromotoluenes, dichlorobenzenes; also, ethylbenzenes from xylenes and propylbenzenes from ethylbenzenes

**Reference:** 3

**Name:** Azoxybenzene *p*-cyano-*p*'-pentyl carbonate (mixed isomers)

**Structure:**



### Thermophysical Properties:

Solid → nematic 96–100°C

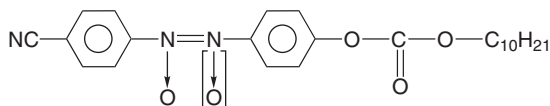
**Analytical Properties:** Separation of disubstituted benzene isomers

**Reference:** 15

### Mesogenic Stationary Phases (continued)

**Name:** Cyanoazoxybenzene decyl carbonate

**Structure:**



**Thermophysical Properties:**

Solid → smectic 74°C

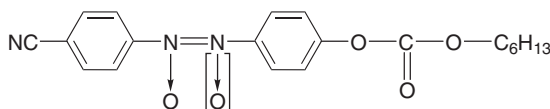
Smectic → isotropic 125.5°C

**Analytical Properties:** Separation of polycyclic hydrocarbons

**Reference:** 16

**Name:** Cyanoazoxybenzene hexyl carbonate (mixed isomers)

**Structure:**



**Thermophysical Properties:**

Solid → nematic 73–76°C

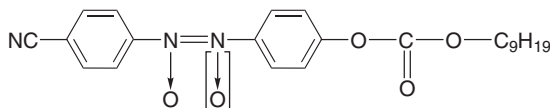
Nematic → isotropic 137°C

**Analytical Properties:** Separation of xylene and ethyltoluene isomers

**Reference:** 16

**Name:** Cyanoazoxybenzene nonyl carbonate (mixed isomers)

**Structure:**



**Thermophysical Properties:**

Solid → smectic 61°C

Smectic → nematic 124°C

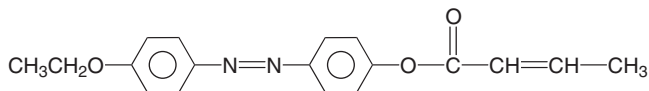
Nematic → isotropic 127°C

**Analytical Properties:** Separation of polycyclic hydrocarbons

**Reference:** 16

**Name:** *p*-(*p*-Ethoxyphenylazo) phenyl crotonate

**Structure:**



**Thermophysical Properties:**

Solid → nematic 110°C

Nematic → isotropic 197°C

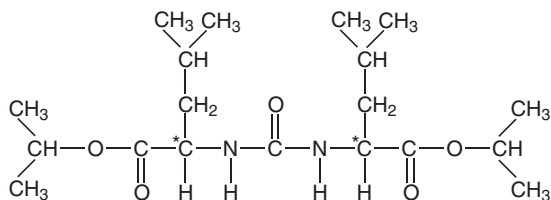
**Analytical Properties:** Separation of aromatic isomers

**Reference:** 12

### Mesogenic Stationary Phases (continued)

**Name:** Carbonyl-*bis*-(D-leucine isopropyl ester)

**Structure:**



**Thermophysical Properties:**

Solid → smectic 55°C

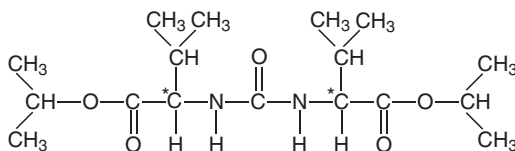
Smectic → isotropic 110°C

**Analytical Properties:** Baseline and near-baseline separations of racemic mixtures of *N*-perfluoroacyl-2-aminoethyl benzenes, trifluoroacetyl (TFA), pentafluoropropionyl (PFP), heptafluorobutyl (HFB)

**Reference:** 17

**Name:** Carbonyl-*bis*-(L-valine isopropyl ester)

**Structure:**



**Thermophysical Properties:**

Solid → smectic<sup>1</sup> 91°C

Smectic<sup>1</sup> → smectic<sup>2</sup> 99°C

Smectic<sup>2</sup> → isotropic 109°C

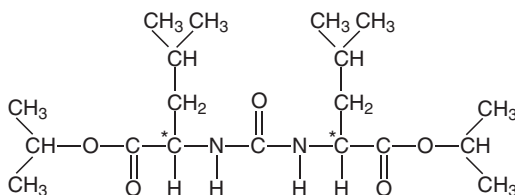
*Note:* This compound exhibits two stable smectic states prior to melting

**Analytical Properties:** Separation of enantiomers

**Reference:** 17

**Name:** Carbonyl-*bis*-(L-valine *t*-butyl ester)

**Structure:**



**Thermophysical Properties:**

Solid → smectic 98°C

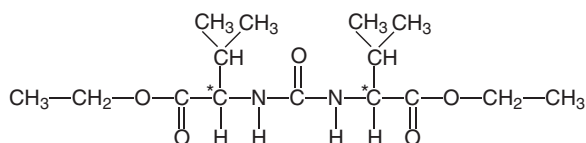
Smectic → isotropic 402°C

**Analytical Properties:** Separation of enantiomers

**Reference:** 17

**Name:** Carbonyl-*bis*-(L-valine ethyl ester)

**Structure:**



## Mesogenic Stationary Phases (continued)

### Thermophysical Properties:

Solid → smectic 88°C

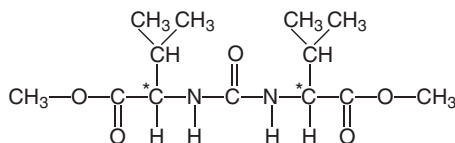
Smectic → isotropic 388°C

**Analytical Properties:** Separation of enantiomers

**Reference:** 17

**Name:** Carbonyl-*bis*-(L-valine methylester)

**Structure:**



### Thermophysical Properties:

Solid → smectic 382°C

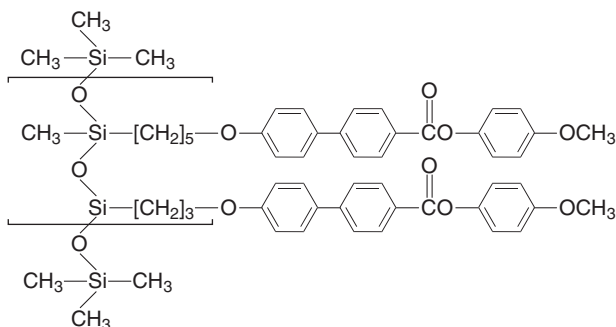
Smectic → isotropic 415°C

**Analytical Properties:** Separation of enantiomers

**Reference:** 17

**Name:** Phenylcarboxylate ester (systematic name not available)

**Structure:**



### Thermophysical Properties:

Solid → smectic 118°C

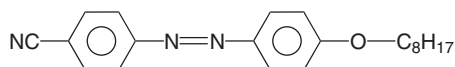
Smectic → isotropic 300°C

**Analytical Properties:** Separation of three- and four-member methylated polycyclic aromatic hydrocarbons (PAHs) on basis of length-to-breadth ratio (*l/b*); as *l/b* increases, retention time decreases; cross-linking increases retention times, separation of methylcrypene isomers

**Reference:** 18

**Name:** *p*-Cyano-*p*'-octoxyazobenzene

**Structure:**



### Thermophysical Properties:

Solid → nematic 101°C

Nematic → isotropic 111°C

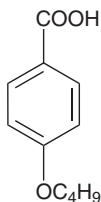
**Analytical Properties:** Separation of ethyltoluenes, chlorotoluenes, bromotoluenes, dichlorobenzenes; also, ethylbenzenes from xylenes and propylbenzene from ethylbenzenes

**Reference:** 3

### Mesogenic Stationary Phases (continued)

**Name:** *p*-*n*-Butoxybenzoic acid

**Structure:**



**Thermophysical properties:**

Solid → 100°C

Mesomorphous → 150°C (not well characterized)

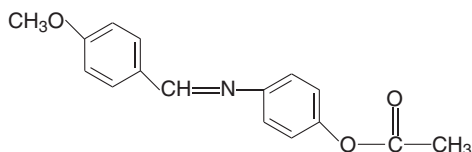
Isotropic → 160°C

**Analytical Properties:** Separation of methyl and monoalkyl substituted benzenes as well as organoelemental compounds (for example, dimethyl mercury)

**Reference:** 19

**Name:** *p*-[(*p*-Methoxybenzylidene)-amino]phenylacetate

**Structure:**



**Thermophysical Properties:**

Solid → nematic 80°C

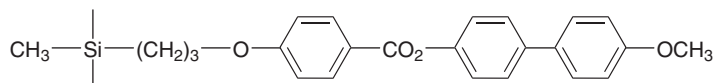
Nematic → isotropic 108°C

**Analytical Properties:** Separation of substituted phenols; selectivity is best at the lower end of the nematic range

**Reference:** 20

**Name:** Poly (mesogen/methyl) siloxane (PMMS) (compound has not been named)

**Structure:**



**Thermophysical Properties:**

Solid → nematic 70°C

Nematic → isotropic 300°C

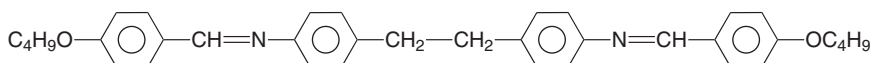
High thermal stability

**Analytical Properties:** Separation of methylchrysene isomers

**Reference:** 21

**Name:** *N,N'*-Bis-(*p*-butoxybenzylidene)-*bis-p*-toluidine (BBBT)

**Structure:**



**Thermophysical Properties:**

Solid → smectic 159°C

Smectic → nematic 188°C

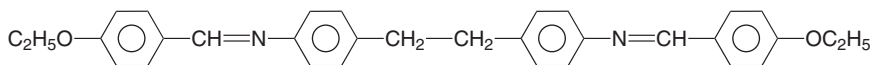
Nematic → isotropic 303°C

### Mesogenic Stationary Phases (continued)

**Analytical Properties:** Separation of polycyclic aromatic hydrocarbons on the basis of length-to-breadth ratio  
**Reference:** 23

**Name:** *N,N'*-Bis-(*p*-ethoxybenzylidene)- $\alpha,\alpha'$ -bi-*p*-toluidine (BEBT)

**Structure:**



**Thermophysical Properties:**

Solid  $\rightarrow$  nematic 173°C

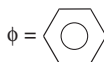
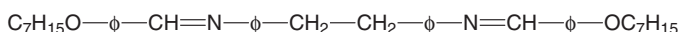
Nematic  $\rightarrow$  isotropic 341°C

**Analytical Properties:** Separation of polynuclear aromatic hydrocarbons

**Reference:** 24

**Name:** *N,N'*-Bis-(*n-p*-heptoxybenzylidene)- $\alpha,\alpha'$ -bi-*p*-toluidine (BH<sub>p</sub>BT)

**Structure:**



**Thermophysical Properties:**

Solid  $\rightarrow$  smectic 119°C

Smectic  $\rightarrow$  nematic 238°C

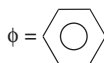
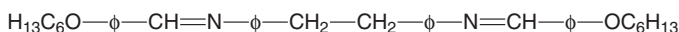
Nematic  $\rightarrow$  isotropic 262°C

**Analytical Properties:** Separation of polynuclear aromatic hydrocarbons

**Reference:** 24

**Name:** *N,N'*-Bis-(*n-p*-hexoxybenzylidene)- $\alpha,\alpha'$ -bi-*p*-toluidine (BH<sub>x</sub>BT)

**Structure:**



**Thermophysical Properties:**

Solid  $\rightarrow$  smectic 127°C

Smectic  $\rightarrow$  nematic 229°C

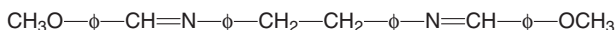
Nematic  $\rightarrow$  isotropic 276°C

**Analytical Properties:** Separation of methyl and nitro derivatives of naphthalene; separation of higher hydrocarbons

**Reference:** 25

**Name:** *N,N'*-Bis-(*p*-methoxybenzylidene)- $\alpha,\alpha'$ -bi-*p*-toluidine (BMBT)

**Structure:**



**Thermophysical Properties:**

Solid  $\rightarrow$  nematic 181°C

Nematic  $\rightarrow$  isotropic 320°C

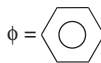
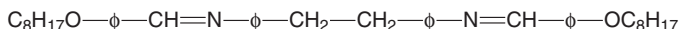
**Analytical Properties:** Separation of androstane and cholestane alcohols and ketones; good separation of azaheterocyclic compounds; column bleed of BMBT can occur during prolonged periods of operation of elevated temperatures

**Reference:** 26

### Mesogenic Stationary Phases (continued)

**Name:** *N,N*-Bis-(*n*-octoxybenzylidene)- $\alpha,\alpha'$ -bi-*p*-toluidine (BoBT)

**Structure:**



**Thermophysical Properties:**

Solid  $\rightarrow$  smectic 118°C

Smectic  $\rightarrow$  nematic 244°C

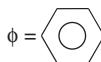
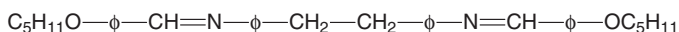
Nematic  $\rightarrow$  isotropic 255°C

**Analytical Properties:** Separation of polynuclear aromatic hydrocarbons

**Reference:** 24

**Name:** *N,N*-Bis-(*p*-*n*-pentoxybenzylidene)- $\alpha,\alpha'$ -bi-*p*-toluidine (BPeBT)

**Structure:**



**Thermophysical Properties:**

Solid  $\rightarrow$  smectic 139°C

Smectic  $\rightarrow$  nematic 208°C

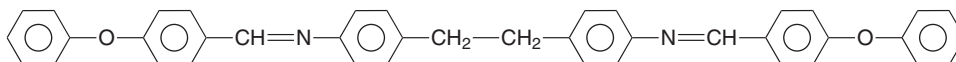
Nematic  $\rightarrow$  isotropic 283°C

**Analytical Properties:** Separation of polynuclear aromatic hydrocarbons

**Reference:** 24

**Name:** *N,N'*-Bis-(*p*-phenylbenzylidene)- $\alpha,\alpha'$ -bi-*p*-toluidine (BphBT)

**Structure:**



**Thermophysical Properties:**

Solid  $\rightarrow$  nematic 257°C

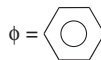
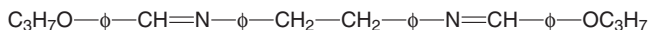
Nematic  $\rightarrow$  isotropic 403°C

**Analytical Properties:** Separation of unadulterated steroids; used chromatographically in the temperature range of 260–270°C

**Reference:** 27

**Name:** *N,N'*-Bis-(*p*-*n*-propoxybenzylidene)- $\alpha,\alpha'$ -bi-*p*-toluidine (BPrBT)

**Structure:**



**Thermophysical Properties:**

Solid  $\rightarrow$  smectic 169°C

Smectic  $\rightarrow$  nematic 176°C

Nematic  $\rightarrow$  isotropic 311°C

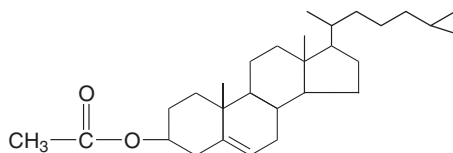
**Analytical Properties:** Separation of polynuclear aromatic hydrocarbons

**Reference:** 24

## Cholesteric Phases

**Name:** Cholesteryl acetate

**Structure:**



**Thermophysical Properties:**

Solid → cholesteric 94.5°C

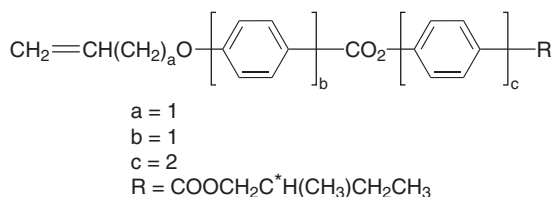
Cholesteric → isotropic 116.5°C

**Analytical Properties:** Separation of aromatics and paraffins

**Reference:** 28

**Name:** (S)-4'-[(2-Methyl-1-butoxy)carbonyl] biphenyl-4-yl 4-(allyloxy) benzoate

**Structure:**



**Thermophysical Properties:**

Solid → smectic 100°C

Smectic → cholesteric 150°C

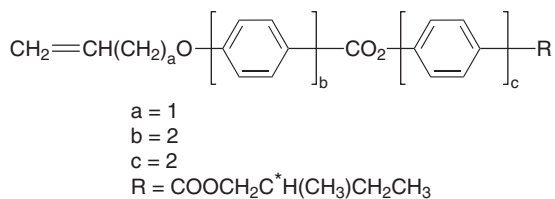
Cholesteric → isotropic 188°C

**Analytical Properties:** Suggested for separation of polycyclic aromatic compounds

**Reference:** 11

**Name:** (S)-4'-[(2-Methyl-1-butoxy)carbonyl] biphenyl-4-yl 4-[4-(allyloxy) phenyl] benzoate

**Structure:**



**Thermophysical Properties:**

Solid → smectic 152°C

Smectic → cholesteric 240°C

Cholesteric → isotropic 278°C

**Analytical Properties:** Suggested for separation of polycyclic aromatic compounds

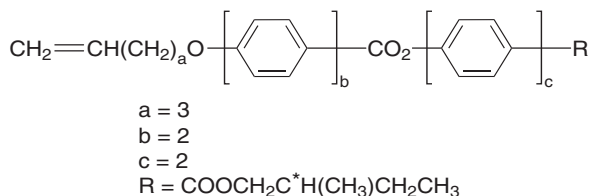
**Reference:** 11



### Cholesteric Phases (continued)

**Name:** (S)-4'-[(2-Methyl-1-butoxy)biphenyl-4-yl 4-(4-4-pentenloxy) phenyl] benzoate

**Structure:**



**Thermophysical Properties:**

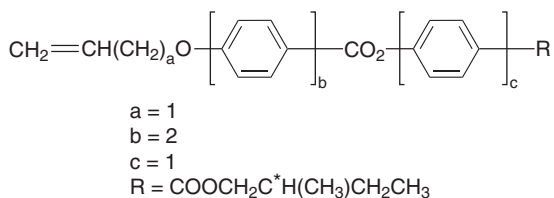
Solid → smectic 135°C  
Smectic → cholesteric 295°C  
Cholesteric → isotropic 315°C

**Analytical Properties:** Suggested for separation of polycyclic aromatic compounds

**Reference:** 11

**Name:** (S)-4-[(2-Methyl-1-butoxy)carbonyl]phenyl-4-[4-(allyloxy)phenyl] benzoate

**Structure:**



**Thermophysical Properties:**

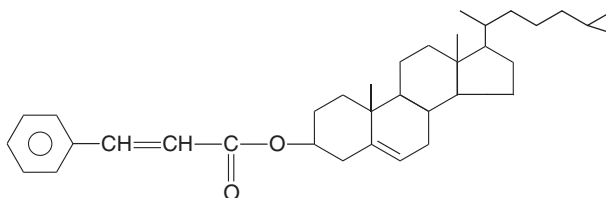
Solid → smectic 118°C  
Smectic → cholesteric 198°C  
Cholesteric → isotropic 213°C

**Analytical Properties:** Suggested for separation of polycyclic aromatic compounds

**Reference:** 11

**Name:** Cholesterol cinnamate

**Structure:**



**Thermophysical Properties:**

Solid → cholesteric 160°C  
Cholesteric → isotropic 210°C

**Analytical Properties:** Separation of olefinic positional isomers

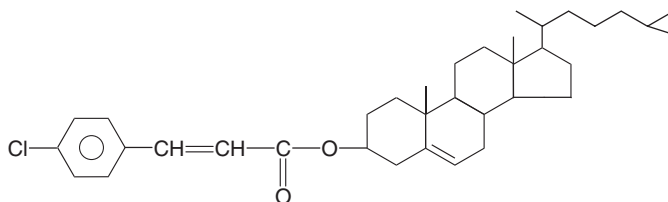
**Reference:** 12, 29

### Cholesteric Phases (continued)

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**Name:** Cholesterol-*p*-chlorocinnamate (CpCC)

**Structure:**



**Thermophysical Properties:**

Solid → cholesteric 144°C

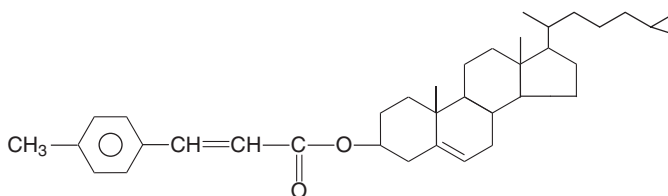
Cholesteric → isotropic 268°C

**Analytical Properties:** Separation of diastereomeric amides and carbamates; the separation of olefinic geometrical isomers is dependent upon the position of the double bond

**Reference:** 29, 30

**Name:** Cholesterol-*p*-methylcinnamate

**Structure:**



**Thermophysical Properties:**

Solid → cholesteric 157°C

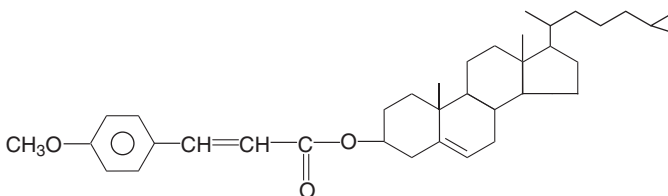
Cholesteric → isotropic 254°C

**Analytical Properties:** Separation of olefinic positional isomers

**Reference:** 29

**Name:** Cholesterol-*p*-methoxycinnamate

**Structure:**



**Thermophysical Properties:**

Solid → cholesteric 165°C

Cholesteric → isotropic 255°C

**Analytical Properties:** Separation of olefinic positional isomers

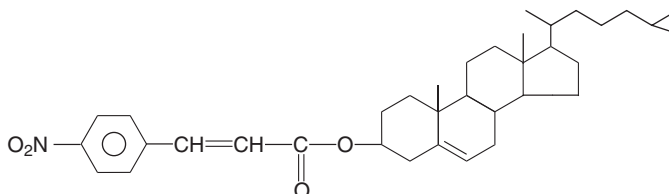
**Reference:** 29

### Cholesteric Phases (continued)

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**Name:** Cholesterol *p*-nitrocinnamate

**Structure:**



**Thermophysical Properties:**

Solid → cholesteric 167°C

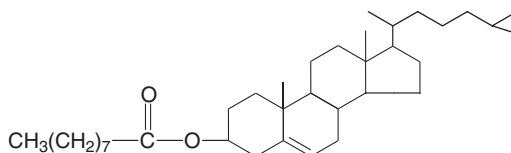
Cholesteric → isotropic 265°C

**Analytical Properties:** Separation of geometrical isomers (2- and 3-octadecene) using *p*-substituted cholesterol; (best separation) *p*-NO<sub>2</sub> > *p*-MeO > cholesterol cinnamate > *p*-Me > *p*-Cl (worst separation) for unsaturation occurring within four carbon atoms from the terminal methyl; the above order holds for separations of tetradecen-1-ol acetates; for unsaturation on carbons 5–12 from the terminal methyl of the tetradecen-1-ol of acetates, the best separation is the reverse of the above

**Reference:** 29

**Name:** Cholesteryl *n*-nonanoate

**Structure:**



**Thermophysical Properties:**

Solid → smectic 77.5°C

Smectic → cholesteric 80.5°C

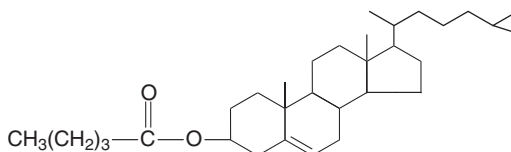
Cholesteric → isotropic 92°C

**Analytical Properties:** Separation of aromatics and paraffins

**Reference:** 28

**Name:** Cholesteryl *n*-valerate

**Structure:**



**Thermophysical Properties:**

Solid → cholesteric 93°C

Cholesteric → isotropic 101.5°C

**Analytical Properties:** Separation of aromatics and paraffins

**Reference:** 28

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## TRAPPING SORBENTS

The following table provides a listing of the major types of sorbents used in sampling, concentrating, odor profiling, and air and water pollution research.<sup>1-6</sup> These materials are useful in a wide variety of research and control applications. Many can be obtained commercially in different sizes, depending on the application involved. The purpose of this table is to aid in the choice of a sorbent for a given analysis. Information that is specific for solid phase microextraction (SPME) is provided elsewhere in this chapter.

## REFERENCES

1. Borgstedt, H.U., Emmel, H.W., Koglin, E., Melcher, R.G., Peters, A., and Sequaris, J.M.L., *Analytical Problems*, Springer-Verlag, Berlin, 1986.
2. Averill, W. and Purcell, J.E., Concentration and gc determination of organic compounds from air and water, *Chromatogr. Newslett.*, 6, 30, 1978.
3. Gallant, R.F., King, J.W., Levins, P.L., and Piecewicz, J.F., Characterization of Sorbent Resins for Use in Environmental Sampling, Report EPA-600/7-78-054, March 1978.
4. Chladek, E. and Marano, R.S., Use of bonded phase silica sorbents for the sampling of priority pollutants in waste waters, *J. Chromatogr. Sci.*, 22, 313, 1984.
5. Good, T.J., Applications of bonded-phase materials, *American Laboratory*, July 1981, p. 36.
6. Beyermann, K., *Organic Trace Analysis*, Halsted Press (of John Wiley & Sons), New York, 1984.

### Trapping Sorbents

Sorbent	Desorption Solvents	Applications
Activated carbon	Carbon disulfide, methylene chloride, diethyl ether, diethyl ether with 1% methanol, diethyl ether with 5% 2-propanol (caution: CS <sub>2</sub> and CH <sub>3</sub> OH can react in the presence of charcoal)	Used for common volatile organics; examples include methylene chloride, vinyl chloride, chlorinated aliphatics, aromatics, acetates; more data are provided in the "Adsorbents for Gas Chromatography" table
<i>Notes:</i> Metallic or salt impurities in the sorbent can sometimes cause the irreversible adsorption of electron-rich oxygen functionalities; examples include 1-butanol, 2-butanone, and 2-ethoxyacetate; recovery rate is often poor for polar compounds		
Graphitized carbon-black	Carbon disulfide, methylene chloride, diethyl ether (or thermal desorption can be used)	Used for common volatile aliphatic and aromatic compounds, organic acids and alcohols, and chlorinated aliphatics; more data are provided in the "Adsorbents for Gas Chromatography" table
<i>Notes:</i> These sorbents are hydrophobic and are not very sensitive to moisture; the possibility of thermal desorption makes them valuable for trace-level analyses		
Silica gel	Methanol, ethanol, water, diethyl ether	Used for polar compound collection and concentration; examples include alcohols, phenols, chlorophenols, chlorinated aromatics, aliphatic and aromatic amines, nitrogen dioxide; more data are provided in the "Adsorbents for Gas Chromatography" table
<i>Notes:</i> Useful for compounds that cannot be recovered from the charcoal sorbents; the most serious problem with silica is the effect of water, which can cause desorption of the analytes of interest, and the heating effect involved can sometimes initiate reactions such as polymerization or hydrolysis of the analyte		
Activated alumina	Water, diethyl ether, methanol	Used for polar compounds such as alcohols, glycols, ketones, aldehydes; has also been used for polychlorinated biphenyls and phthalates; more data are provided in the "Adsorbents for Gas Chromatography" table
<i>Notes:</i> Similar in application to silica gel		
Porous polymers	Hexane, diethyl ether, alcohols (thermal desorption also possible in some cases)	Used for a wide range of compounds, including phenols, acidic and basic organics, pesticides, priority pollutants; more data are provided in the "Porous Polymer Phases" table
<i>Notes:</i> The most commonly used porous polymer sorbent is Tenax-GC, although the Porapak and Chromosorb Century series have also been used; Tenax-GC has been used with thermal desorption methods, but can release toluene, benzene, and trichloroethylene residues at higher temperatures; in addition to Tenax-GC, XAD 2-8, Porapak-N, and Chromosorbs 101, 102, 103, and 106 have found applications, sometimes in "stacked" sampling devices (for example, a sorbent column of Tenax-GC — Chromosorb 106 in tandem); Chromosorb 106, a very low polarity polymer, has the lowest retention of water with respect to organic materials and is well suited for use as a backup sorbent		
Bonded phases	Methanol, hexane, diethyl ether	Used for specialized applications in pesticides, herbicides, and polynuclear aromatic hydrocarbons
<i>Notes:</i> Most expensive of the common sorbents; useful for the collection of organic samples from water		
Molecular sieves	Carbon disulfide, hexane diethyl ether	Used for the collection of aldehydes, alcohols, and acrolein
<i>Notes:</i> Molecular sieve 13-X is the main molecular sieve to be used as a trapping adsorbent; the sorbents will also retain water		

## SORBENTS FOR THE SEPARATION OF VOLATILE INORGANIC SPECIES

The following sorbents have proven useful for the adsorptive separation of volatile inorganic species.<sup>1</sup>

### REFERENCES

1. MacDonald, J.C., *Inorganic Chromatographic Analysis: Chemical Analysis Series*, Vol. 78, John Wiley & Sons, New York, 1985.

**Sorbents for the Separation of Volatile Inorganic Species**

Separation Material	Typical Separations
Alumina	O <sub>2</sub> , N <sub>2</sub> , CO <sub>2</sub>
Beryllium oxide	H <sub>2</sub> S, H <sub>2</sub> O, NH <sub>3</sub>
Silica gel	O <sub>2</sub> /N <sub>2</sub> , CO <sub>2</sub> , O <sub>3</sub> , H <sub>2</sub> S, SO <sub>2</sub>
Chromium(III) oxide	O <sub>2</sub> , N <sub>2</sub> , Ar, He
Clay minerals (Attapulgit, Sepiolite)	O <sub>2</sub> , N <sub>2</sub> , CO, CO <sub>2</sub>
Kaolin	He, O <sub>2</sub> , N <sub>2</sub> , CO, CO <sub>2</sub>
Sodium-, lithium fluoride, alumina	MoF <sub>6</sub> , SbF <sub>5</sub> , UF <sub>6</sub> , F
Quartz granules	Ta, Re, Ru, Os, Ir: oxides, hydroxides
Chromosorb 102	Element hydrides
Graphite	NH <sub>3</sub> , N <sub>2</sub> , H <sub>2</sub>
Synthetic diamond	CF <sub>2</sub> O, CO <sub>2</sub>
Molecular sieve	Hydrogen isotopes
Carbon molecular sieve	O <sub>2</sub> , N <sub>2</sub> , CO, CO <sub>2</sub> , N <sub>2</sub> O, SO <sub>2</sub> , H <sub>2</sub> S
XAD resins	NH <sub>3</sub> , SO <sub>2</sub> , H <sub>2</sub> S, CO, CO <sub>2</sub> , H <sub>2</sub> O
Porapak Q	GeH <sub>4</sub> , SnH <sub>4</sub> , AsH <sub>3</sub> , SbH <sub>3</sub> , Sn(CH <sub>3</sub> ) <sub>4</sub>
Porapak QS polymers	H <sub>2</sub> S, CH <sub>3</sub> SH, (CH <sub>3</sub> ) <sub>2</sub> S, (CH <sub>3</sub> ) <sub>2</sub> S <sub>X</sub> , SO <sub>2</sub>
Porapak P	Chlorides of Si, Sn, Ge, P, As, Ti, V, Sb
Teflon	F, MoF <sub>6</sub> , SbF <sub>5</sub> , SbF <sub>3</sub>

From MacDonald, J.C., *Inorganic Chromatographic Analysis: Chemical Analysis Series*, Vol. 78, John Wiley & Sons, New York, 1985. With permission.

## ACTIVATED CARBON AS A TRAPPING SORBENT FOR TRACE METALS

Activated carbon, which is a common trapping sorbent for organic species, can also be used for trace metals.<sup>1</sup> This material is typically used by passing the samples through a thin layer (50 to 150 mg) of the activated carbon that is supported on a filter disk. It can also be used by shaking 50 to 150 mg of activated carbon in the solution containing the heavy metal, and then filtering the sorbent out of the solution.

## REFERENCES

1. Alfasi, Z.B. and Wai, C.M., *Preconcentration Techniques for Trace Elements*, CRC Press, Boca Raton, FL, 1992.

**Activated Carbon as a Trapping Sorbent for Trace Metals**

Matrices	Trace Metals	Complexing Agents
Water	Ag, Bi, Cd, Co, Cu, Fe, In, Mg, Mn, Ni, Pb, Zn	(NaOH; pH 7–8)
Water	Ag, As, Ca, Cd, Ce, Co, Cu, Dy, Fe, La, Mg, Mn, Nb, Nd, Ni, Pb, Pr, Sb, Sc, Sn, U, V, Y, Zn	8-Quinolinol
Water	Ba, Co, Cs, Eu, Mn, Zn	APDC, DDTC, PAN, 8-quinolinol
Water	Hg, methyl mercury	—
Water	Hg (halide)	—
Water	Hg (halide)	—
Water	U	L-ascorbic acid
HNO <sub>3</sub> , water, Al, KCl	Ag, Bi, Cd, Cu, Hg, Pb, Zn	Dithizone
Mn, MnO <sub>3</sub> , Mn salts	Bi, Cd, Co, Cu, Fe, In, Ni, Pb, Ti, Zn	Ethyl xanthate
Co, Co(NO <sub>3</sub> ) <sub>2</sub>	Ag, Bi	APDC
Ni, Ni(NO <sub>3</sub> ) <sub>2</sub>	Ag, Bi	APDC
Mg, Mg(NO <sub>3</sub> ) <sub>2</sub>	Ag, Cu, Fe, Hg, In, Mn, Pb, Zn	(pH 8.1–9)
Al	Cd, Co, Cu, Ni, Pb	Thioacetamide
Ag, TINO <sub>3</sub>	Bi, Co, Cu, Fe, In, Pb	Xenol orange
Cr salts	Ag, Bi, Cd, Co, Cu, In, Ni, Pb, Ti, Zn	HAHDTC
Co, In, Pb, Ni, Zn	Ag, Bi, Cu, Ti	DDTC
Se	Cd, Co, Cu, Fe, Ni, Pb, Zn	DDTC
NaClO <sub>4</sub>	Ag, Bi, Cd, Co, Cu, Fe, Hg, In, Mn, Ni, Pb	(pH 6)

*Note:* APDC = ammonium pyrrolidinecarbodithiolate; DDTC = diethyldithiocarbamate; HAH-DTC = hexamethyleneammonium hexaethylenedithiocarbamate; PAN = 1-(2-pyridyl-lazo)-2-naphthol.

## REAGENT IMPREGNATED RESINS AS TRAPPING SORBENTS FOR TRACE MINERALS

Reagent impregnated resins can be used as trapping sorbents for the preconcentration of heavy metals.<sup>1</sup> These materials can be used in the same way as activated carbons.

### REFERENCES

1. Alfasi, Z.B. and Wai, C.M., *Preconcentration Techniques for Trace Elements*, CRC Press, Boca Raton, FL, 1992.

**Reagent Impregnated Resins as Trapping Sorbents for Trace Minerals**

Reagents	Adsorbents	Metals
TBP	Porous polystyrene DVB resins	U
YBP	Levextrel (polystyrene DVB resins)	U
DEHPA	Levextrel	Zn
DEHPA	XAD-2	Zn
Alamine 336	XAD-2	U
LIX-63	XAD-2	Co, Cu, Fe, Ni, etc.
LIX-64N, -65N	XAD-2	Cu
Hydroxyoximes	XAD-2	Cu
Kelex 100	XAD-2	Co, Cu, Fe, Ni
Kelex 100	XAD-2, -4, -7, -8, -11	Cu
Dithizone, STTA	Polystyrene DVB resins	Hg
Dithizone (acetone)	XAD-1, -2, -4, -7, -8	Hg, methyl mercury
DMABR	XAD-4	Au
Pyrocatechol violet	XAD-2	In, Pb
TPTZ	XAD-2	Co, Cu, Fe, Ni, Zn

*Note:* TBP = tributyl phosphate; DEHPA = diethylhexyl phosphoric acid; STTA = monothio-thenolytrifluoroacetone; DMABR = 5-(4-dimethylaminobenzylidene)-rhodanine; TPTZ = 2,4,6-tri(2-pyridyl)-1,3,5-triazine; LIX 63 = aliphatic  $\alpha$ -hydroxyoxime; LIX 65N = 2-hydroxy-5-nonylbenzophenoneoxime; LIX 64N = a mixture of LIX 65N with approximately 1% (v/v) of LIX-63.



## REAGENT IMPREGNATED FOAMS AS TRAPPING SORBENTS FOR INORGANIC SPECIES

Reagent impregnated foams can be used as trapping sorbents for the preconcentration of heavy metals.<sup>1</sup> These materials can be used in the same way as activated carbons.

### REFERENCES

1. Alfasi, Z.B. and Wai, C.M., *Preconcentration Techniques for Trace Elements*, CRC Press, Boca Raton, FL, 1992.

Reagent Impregnated Foams as Trapping Sorbents for Inorganic Species				
Matrices	Elements	Concentration	Foam Type	Reagents
Water	<sup>131</sup> I, <sup>203</sup> Hg	Traces	Polyether	Alamine 336
Natural water				
Water	Bi, Cd, Co, Cu, Fe, Hg, Ni, Pb, Sn, Zn	Traces	Polyether	Amberlite LA-2
Water	Co, Fe, Mn	Traces to µg/L	Polyether	PAN
Natural water	Cd	µg/L	Polyether	PAN
Water	Au, Hg	µg/L	Polyether	PAN
Water	Ni	Traces to µg/L	—	DMG, α-benzylidioxime
Water	Cr	µg/L	Polyether	DPC
Water	Hg, methyl-Hg, phenyl-Hg	µg/L	Polyether	DADTC
Natural water	Sn	Traces	Polyether	Toluene-3,4-dithiol
Water	Cd, Co, Fe, Ni	Traces	Polyether	Aliquot
Water	Th	Traces	Polyether	PMBP
				HDEHP-TBP
Water	PO <sub>4</sub> <sup>3-</sup>	Traces		Amine-molybdate-TBP

*Note:* PAN = 1-(2-pyridylazo)-2-naphthol; DMG = dimethylglyoxime; DPC = 1,5-diphenylcarbazine; DADTC = diethylammonium diethyldithiocarbamate; PMBP = 1-phenyl-3-methyl-4-benzoyl-pyrazolone-5; HDEHP = *bis*-[2-ethylhexyl]phosphate; TBP = tributyl phosphate.

## CHELATING AGENTS FOR THE ANALYSIS OF INORGANICS BY GAS CHROMATOGRAPHY

The following table provides guidance in choosing a chelating agent for the analysis of inorganic species by gas chromatography.<sup>1-3</sup> The key to the abbreviation list is provided below.

### REFERENCES

1. Guiochon, G. and Pommier, C., *Gas Chromatography of Inorganics and Organometallics*, Ann Arbor Science Publishers, Ann Arbor, MI, 1973.
2. Robards, K., Patsalides, E., and Dilli, S., Review: gas chromatography of metal beta-diketonates and their analogues, *J. Chromatogr.*, 41, 1, 1987.
3. Robards, K. and Patsalides, E., Comparison of the liquid and gas chromatography of five classes of metal complexes, *J. Chromatogr. A*, 844, 181, 1999.

acac	=	acetylacetonate
dibm	=	2,6-dimethyl-3,5-heptanedionate
fod	=	1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionate
hfa	=	hexafluoroacetylacetonate
tacac	=	monothioacetylacetonate
tfa	=	trifluoroacetylacetonate
thd	=	2,2,6,6-tetramethyl-3,5-heptadionate
tpm	=	1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedionate

Aluminum	
In Mixture With	Complex
Be, Sc	acac
Be	acac
Cr	acac
Be, Cr	acac
Be, Sc	tfa
Be, Rh	tfa
Cr, Rh	tfa
Cr, Rh	tfa
Cu, Fe	tfa
Ga, In	tfa
Fe	tfa
Cr, Rh, Zr	tfa
Be, Ga, In, Ti	tfa
Be, Cr	hfa
Be, Cr, Cu	hfa
Be, Cr, Fe	hfa
Be, Cu, Cr, Fe, Pd, Y	fod
Cr, Fe	tpm
Cr, Fe, Cu	tpm
Be, Cr, Fe, Ni	dibm
Traces on U	tfa
Traces	tfa, hfa

Beryllium	
In Mixture With	Complex
Al, Sc	acac
Cu	acac
Al, Cr	acac
Al, Sc	tfa
Al, Ga, Ti, In	tfa
Al, Cr	hfa
Al, Cr, Cu	hfa
Al, Cr, Fe	hfa
Al, Cu, Cr, Fe, Pd, Y	fod
Al, Cr, Fe, Ni	dibm
Traces	tfa

Chromium	
In Mixture With	Complex
Al, Be	acac
Al	acac
Al, Rh	tfa
Al, Rh, Zr	tfa
Al, Be	hfa
Al, Be, Cu	hfa
Al, Be, Fe	hfa
Fe, Rh	hfa
Ru	hfa, tpm
Al, Fe	tpm
Al, Fe, Cu	tpm
Al, Be, Cu, Fe, Pd, Y	fod
Al, Be, Fe, Ni	dibm
Traces in Fe	tfa
Traces	tfa, hfa

Copper	
In Mixture With	Complex
Be	acac
Al, Fe	tfa
Fe	tfa
Al, Be, Cr	hfa
Fe	hfa
Al, Cr, Fe	tpm
Al, Be, Cr, Fe, Pd, Y	fod

Indium	
In Mixture With	Complex
Al, Ga	tfa
Al, Be, Ga, Tl	tfa

Nickel	
In Mixture With	Complex
Co, Pd	tacac
Al, Be, Cr, Fe	dibm

Cobalt	
In Mixture With	Complex
Ru	tfa, hfa
Ni, Pd	tacac
Traces	fod

Gallium	
In Mixture With	Complex
Al, In	tfa
Al, Be, In, Tl	tfa

Iron	
In Mixture With	Complex
Al, Cu	tfa
Al	tfa
Cr	tfa
Cu	tfa
Al, Be, Cr	hfa
Cu	hfa
Cr, Rh	hfa
Al, Cr	tpm
Al, Cr, Cu	tpm
Al, Be, Cr, Cu, Pd, Y	fod
Al, Be, Cr, Ni	dibm

Paladium	
In Mixture With	Complex
A, Be, Cr, Cu, Fe, Y	fod
Co, Ni	tacac

Rare Earths	
In Mixture With	Complex
Sc	thd
Sc, Y	tpm
Sc, Y	fod
Other rare earths	hfa + tributylphosphate

Ruthenium	
In Mixture With	Complex
Co	tfa, hfa
Cr	hfa

Thallium	
In Mixture With	Complex
Al, Be, Ga, In	tfa

Uranium	
In Mixture With	Complex
Th	fod

Zirconium	
In Mixture With	Complex
Al, Cr, Rh	tfa

Rhodium	
In Mixture With	Complex
Al, Cr	tfa
Al, Cr	tfa
Al, Cr, Zr	tfa
Cr, Fe	hfa
Traces	tfa

Scandium	
In Mixture With	Complex
Al, Be	acac
Al, Be	tfa
Rare earths	thd
Rare earths, Y	tpm
Rare earths, Y	fod

Thorium	
In Mixture With	Complex
U	fod

Yttrium	
In Mixture With	Complex
Sc, rare earths	tpm
Sc, rare earths	fod
Al, Be, Cr, Cu, Fe, Pd	fod

## BONDED PHASE MODIFIED SILICA SUBSTRATES FOR SOLID PHASE EXTRACTION

The following table provides the most commonly used bonded phase modified silica substrates in solid phase extraction.<sup>1</sup> Additional information on many of these materials can be found in the “More Common HPLC Stationary Phases” table in the HPLC chapter in this book.

### REFERENCES

1. Fritz, J.S., *Solid Phase Extraction*, Wiley-VCH, New York, 1999.

Bonded Phase Modified Silica Substrates for Solid Phase Extraction		
Phase	Polarity of Phase	Designation
Octadecyl, endcapped	Strongly apolar	C18ec
Octadecyl	Strongly apolar	C18
Octyl	Apolar	C8
Ethyl	Slightly polar	C2
Cyclohexyl	Slightly polar	CH
Phenyl	Slightly polar	PH
Cyanopropyl	Polar	CN
Diol	Polar	2OH
Silica gel	Polar	SiOH
Carboxymethyl	Weak cation exchanger	CBA
Aminopropyl	Weak anion exchanger	NH <sub>2</sub>
Propylbenzene sulfonic acid	Strong cation exchanger	SCX
Trimethylaminopropyl	Strong anion exchanger	SAX

From Fritz, J.S., *Solid Phase Extraction*, Wiley-VCH, New York, 1999. With permission.

## SOLID PHASE MICROEXTRACTION SORBENTS

The following tables provide information on the selection and optimization of solid phase microextraction fibers.<sup>1</sup> The reader is also advised to consult the tables for headspace analysis in this chapter.

### REFERENCES

1. Shirey, R., Supelco Corp., Bellefonte, PA, 2003 (private communication).

### FIBER SELECTION CRITERIA

The main fiber selection parameters are polarity and relative molecular mass (RMM). This table provides general guidelines on the applicability of available fibers relative to these two parameters. The fibers are characterized by the extraction mechanism, either adsorption or absorption. Adsorbent fibers contain particles suspended in PDMS or Carbowax.

**Fiber Selection Criteria**

Fiber	Type of Fiber	Polarity	RMM Range
7- $\mu$ m PDMS	Absorbent	Nonpolar	150–700
30- $\mu$ m PDMS	Absorbent	Nonpolar	80–600
85- $\mu$ m polyacrylate	Absorbent	Polar	60–450
100- $\mu$ m PDMS	Absorbent	Nonpolar	55–400
PDMS-DVB	Adsorbent	Bipolar	50–350
Carbowax-DVB	Adsorbent	Polar	50–350
PDMS-DVB-Carboxen	Adsorbent	Bipolar	40–270
PDMS-Carboxen	Adsorbent	Bipolar	35–180

*Note:* PDMS = polydimethylsiloxane; DVB = divinylbenzene (3- to 5- $\mu$ m particles); Carboxen = Carboxen 1006 (contains micro-, meso-, and macro-tapered pores; 3- to 5- $\mu$ m particles). RMM range is ideal range for optimum extraction. Ranges can be extended by varying extraction times, but results will not be optimized.

## EXTRACTION CAPABILITY OF SOLID PHASE MICROEXTRACTION SORBENTS

This table shows the extraction capability of the fibers for acetone, a small, moderately polar analyte; 4-nitrophenol, a medium-size polar analyte; and benzo(GHI)perylene, a large nonpolar analyte. It provides a general guideline for fiber selection.

Extraction Capability of Solid Phase Microextraction Sorbents			
Fiber	Approximate Linear Concentration Range of Acetone, 10-Min Ext (FID)	Approximate Linear Concentration Range of 4-Nitrophenol, 20-Min Ext (GC/MS)	Approximate Linear Concentration Range of Benzo(GHI)perylene, 20-Min Ext
7- $\mu$ m PDMS	100 ppm and up	Not extracted	100 ppt–500 ppb
30- $\mu$ m PDMS	10 ppm and up	10 ppm and up	100 ppt–10 ppm
85- $\mu$ m polyacrylate	1–1000 ppm	5 ppb–100 ppm	500 ppt–10 ppm
100- $\mu$ m PDMS	500 ppb–1000 ppm	500 ppb–500 ppm	500 ppt–10 ppm
PDMS-DVB	50 ppb–100 ppm	25 ppb–10 ppm	10 ppb–1 ppm
Carbowax-DVB	100 ppb–100 ppm	5 ppb–10 ppm	50 ppb–5 ppm
PDMS-DVB-Carboxen	25 ppb–10 ppm	50 ppb–10 ppm	100 ppb–1 ppm poorly desorbed
PDMS-Carboxen	5 ppb–5 ppm	100 ppb–10 ppm	Not desorbed

*Note:* 1 ppm = 1 part in  $1 \times 10^6$ ; 1 ppb = 1 part in  $1 \times 10^9$ ; 1 ppt = 1 part in  $1 \times 10^{12}$ .

## SALTING OUT REAGENTS FOR HEADSPACE ANALYSIS

The following table provides data on the common salts used for salting out in chromatographic headspace analysis, as applied to direct injection methods and to solid phase microextraction.<sup>1,2</sup> Data are provided for the most commonly available salts, although others are possible. Sodium citrate, for example, occurs as the dihydrate and the pentahydrate. The pentahydrate is not as stable as the dihydrate, however, and dries out on exposure to air, forming cakes. Potassium carbonate occurs as the dihydrate, trihydrate, and sesquihydrate; however, data are provided only for the anhydrous material. The solubility is provided as the number of grams that can dissolve in 100 ml of water at the indicated temperature. The vapor enhancement cited is the degree of increase of the concentration of vapor over the solution of a 2% (mass/mass) ethanol solution in water at 60°C.<sup>3</sup>

## REFERENCES

1. Lide, D.R., Ed., *CRC Handbook of Chemistry and Physics*, 83rd ed., CRC Press, Boca Raton, FL, 2002.
2. *NIST Web Book*, [www.webbook.nist.gov/chemistry/](http://www.webbook.nist.gov/chemistry/), 2003.
3. Ioffe, B.V. and Vitenberg, A.G., *Head Space Analysis and Related Methods in Gas Chromatography*, Wiley Interscience, New York, 1983.

**Salting Out Reagents for Headspace Analysis**

Salt	Formula	Relative Molecular Mass	Density	Solubility		Vapor Enhancement
				Cold Water	Hot Water	
Potassium carbonate	K <sub>2</sub> CO <sub>3</sub>	138.21	2.428 at 14°C	112 <sup>a</sup>	156 <sup>b</sup>	8
Ammonium sulfate	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	132.13	1.769 at 50°C	70.6 <sup>c</sup>	103.8 <sup>b</sup>	5
Sodium citrate (dihydrate)	Na <sub>3</sub> C <sub>6</sub> H <sub>5</sub> O <sub>7</sub> ·2H <sub>2</sub> O	294.10		72 <sup>d</sup>	167 <sup>b</sup>	5
Sodium chloride	NaCl	58.44	2.165 <sup>e</sup>	37.5 <sup>a</sup>	39.12 <sup>b</sup>	3
Ammonium chloride	NH <sub>4</sub> Cl	53.49	1.527	29.7 <sup>c</sup>	75.8 <sup>b</sup>	2

<sup>a</sup> 20°C.

<sup>b</sup> 100°C.

<sup>c</sup> 0°C.

<sup>d</sup> 25°C.

<sup>e</sup> Specific gravity, 25/4°C.



## PARTITION COEFFICIENTS OF COMMON FLUIDS IN AIR–WATER SYSTEMS

The following table provides the partition coefficients (or distribution coefficients),  $K = C_s/C_v$  (solid/vapor), at various temperatures, for application in gas chromatographic headspace analysis.<sup>1,2</sup> The values marked with an asterisk were determined from a linear regression of experimental data.

### REFERENCES

1. Ioffe, B.V. and Vitenberg, A.G., *Head Space Analysis and Related Methods in Gas Chromatography*, Wiley Interscience, New York, 1983.
2. Kolb, B. and Ettre, L.S., *Static Headspace Gas Chromatography: Theory and Practice*, Wiley-VCH, New York, 1996.

Partition Coefficient, K						
Fluid	20°C	25°C	30°C	40°C	50°C	60°C
Cyclohexane				0.077	0.055*	0.040
<i>n</i> -Hexane				0.14	0.068*	0.043
Tetrachloroethylene				1.48	1.28*	1.27
1,1,1-Trichloromethane				1.65	1.53*	1.47
<i>o</i> -Xylene				2.44	1.79*	1.31
Toluene	4.6	3.6	2.9	2.82	2.23*	1.77
Benzene	4.8	4.0	3.4	2.90	3.18*	2.27
Dichloromethane				5.65	4.29*	3.31
<i>n</i> -Butyl acetate	126	87	59	31.4	20.6*	13.6
Ethyl acetate	210	150	108	62.4	42.7*	29.3
Methyl ethyl ketone	600	380	283	139.5	109*	68.8
<i>n</i> -Butanol	4660	3600	2710	647	384*	238
Ethanol	7020	5260	4440	1355	820*	511
Dioxane	8000	5750	4330	1618	1002*	624
<i>m</i> -Xylene	5.9	4.0	3.9			
<i>n</i> -Propanol	5480	4090	3210		479*	
Acetone	752	551	484			

## VAPOR PRESSURE AND DENSITY OF SATURATED WATER VAPOR

The following table provides the temperature dependence of the saturated vapor pressure and vapor density of water. This information is useful in gas chromatographic headspace analysis and for SPME sampling.<sup>1,2</sup>

### REFERENCES

1. Kolb, B. and Ettre, L.S., *Static Headspace Gas Chromatography: Theory and Practice*, Wiley-VCH, New York, 1997.
2. Lide, D.R., Ed., *CRC Handbook of Chemistry and Physics*, 83rd ed., CRC Press, Boca Raton, FL, 2002.

Vapor Pressure and Density of Saturated Water Vapor

°C	$p^\circ$ (kPa)	$p^\circ$ (torr)	$d$ (μg/ml)
10	1.2	9.2	9.4
20	2.3	17.5	17.3
30	4.2	31.8	30.3
40	7.4	55.3	51.1
50	12.3	92.5	83.2
60	19.9	149.4	130.5
70	31.1	233.7	198.4
80	47.2	355.1	293.8
90	69.9	525.8	424.1
100	101.1	760.0	598.0
110	142.9	1074.5	826.5
120	198.1	1489.1	1122.0

## DERIVATIZING REAGENTS FOR GAS CHROMATOGRAPHY

The following table lists some of the more common derivatizing reagents used in gas chromatography for (1) increasing sample volatility, (2) increasing sample thermal stability, (3) reducing sample-support interactions, and (4) increasing sensitivity toward a particular detector. The table is divided into reagents for acylation, alkylation, esterification, pentafluorophenylation, and silylation. The conditions and concentrations used in derivatization must be carefully considered, since one can often cause more problems than one cures using these methods. Such problems include poor peak resolution, incomplete reactions and side products, and less than stoichiometric yields of products. Refer to the citation list for more details on the reagents, conditions, and difficulties.

## REFERENCES

### General References

1. Blau, K. and King, G.S., Eds., *Handbook of Derivatives for Chromatography*, Heyden, London, 1978.
2. Knapp, D.R., *Handbook of Analytical Derivatization Reactions*, John Wiley & Sons, New York, 1979.
3. Drozd, J., *Chemical Derivatization in Gas Chromatography*, Elsevier, Amsterdam, 1981.
4. Poole, C.F. and Schutte, S.A., *Contemporary Practice of Chromatography*, Elsevier, Amsterdam, 1984.
5. Grob, R.L., *Modern Practice of Gas Chromatography*, John Wiley & Sons, New York, 1985.
6. Braithwaite, A. and Smith, F.J., *Chromatographic Methods*, Chapman & Hall, London, 1985.
7. Merritt, C., in *Ancillary Techniques of Gas Chromatography*, Ettre, L.S. and McFadder, W.H., Eds., Wiley Interscience, New York, 1969.
8. Hammarstrand, K. and Bonelli, E.J., *Derivative Formation in Gas Chromatography*, Varian Aerograph, Walnut Creek, CA, 1968.
9. Vanden Heuvel, W.J.A., *Gas Chromatography of Steroids in Biological Fluids*, Plenum Press, New York, 1965.

### Acylating Reagents

1. Brooks, C.J.W. and Horning, E.C., Gas chromatographic studies of catecholamines, tryptamines, and other biological amines, *Anal. Chem.*, 36, 1540, 1964.
2. Imai, K., Sugiura, M., and Tamura, Z., Catecholamines in rat tissues and serum determined by gas chromatographic method, *Chem. Pharm. Bull.*, 19, 409, 1971.
3. Scoggins, M.W., Skurcenski, L., and Weinberg, D.S., Gas chromatographic analysis of geometric diamine isomers as tetramethyl derivatives, *J. Chromatogr. Sci.*, 10, 678, 1972.

### Esterification Reagents

1. Shulgin, A.T., Separation and analysis of methylated phenols as their trifluoroacetate ester derivatives, *Anal. Chem.*, 36, 920, 1964.
2. Argauer, R.J., Rapid procedure for the chloroacetylation of microgram quantities of phenols and detection by electron capture gas chromatography, *Anal. Chem.*, 40, 122, 1968.
3. Vanden Heuvel, W.J.A., Gardiner, W.L., and Horning, E.C., Characterization and separation of amines by gas chromatography, *Anal. Chem.*, 36, 1550, 1964.
4. Änggård, E. and Göran, S., Gas chromatography of catecholamine metabolites using electron capture detection and mass spectrometry, *Anal. Chem.*, 41, 1250, 1969.
5. Alley, C.C., Brooks, J.B., and Choudhary, G., Electron capture gas-liquid chromatography of short chain acids as their 2,2,2-trichloroethyl esters, *Anal. Chem.*, 48, 387, 1976.
6. Godse, D.D., Warsh, J.J., and Stancer, H.C., Analysis of acidic monoamine metabolites by gas chromatography-mass spectrometry, *Anal. Chem.*, 49, 915, 1977.

7. Matin, S.B. and Rowland, M., Electron-capture sensitivity comparison of various derivatives of primary and secondary amines, *J. Pharm. Sci.*, 61, 1235, 1972.
8. Bertani, L.M., Dziedzic, S.W., Clarke, D.D., and Gitlow, S.E., A gas-liquid chromatographic method for the separation and quantitation of nomethanephine and methanephine in human urine, *Clin. Chem. Acta*, 30, 227, 1970.
9. Kawai, S. and Tamura, Z., Gas chromatography of catecholamines as their trifluoroacetates, *Chem. Pharm. Bull.*, 16, 699, 1968.
10. Moffat, A.C. and Horning, E.C., A new derivative for the gas-liquid chromatography of picogram quantities of primary amines of the catecholamine series, *Biochem. Biophys. Acta*, 222, 248, 1970.
11. Lamparski, L.I. and Nestruck, T.J., Determination of trace phenols in water by gas chromatographic analysis of heptafluorobutyl derivatives, *J. Chromatogr.*, 156, 143, 1978.
12. Mierzwa, S. and Witek, S., Gas-liquid chromatographic method with electron-capture detection for the determination of residues of some phenoxyacetic acid herbicides in water as their 2,2-trichloroethyl esters, *J. Chromatogr.*, 136, 105, 1977.
13. Hoshika, Y., Gas chromatographic separation of lower aliphatic primary amines as their sulfur-containing schiff bases using a glass capillary column, *J. Chromatogr.*, 136, 253, 1977.
14. Brooks, J.B., Alley, C.C., and Liddle, J.A., Simultaneous esterification of carboxyl and hydroxyl groups with alcohols and heptafluorobutyric anhydride for analysis by gas chromatography, *Anal. Chem.*, 46, 1930, 1974.
15. Deyrup, C.L., Chang, S.M., Weintraub, R.A., and Moye, H.A., Simultaneous esterification and acylation of pesticides for analysis by gas chromatography. 1. Derivatization of glyphosate and (amino-methyl) phosphonic acid with fluorinated alcohols-perfluorinated anhydrides, *J. Agric. Food Chem.*, 33, 944, 1985.
16. Samar, A.M., Andrieu, J.L., Bacconin, A., Fugier, J.C., Herilier, H., and Faucon, G., Assay of lipids in dog myocardium using capillary gas chromatography and derivatization with boron trifluoride and methanols, *J. Chromatogr.*, 339, 25, 1985.

## Pentafluorobenzoyl Reagents

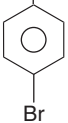
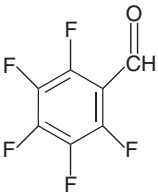
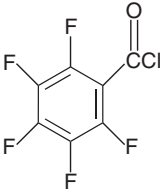
1. Mosier, A.R., Andre, C.E., and Viets, F.G., Jr., Identification of aliphatic amines volatilized from cattle feedyard, *Environ. Sci. Technol.*, 7, 642, 1973.
2. DeBeer, J., Van Petegham, C., and Heyndridex, Al., Electron capture-gas-liquid chromatography (EC-GLC) determination of the herbicidal monohalogenated phenoxyalkyl acid mecoprop in tissues, urine and plasma after derivatization with pentafluorobenzylbromide, *Vet. Hum. Toxicol.*, 21, 172, 1979.
3. Davis, B., Crown ether catalyzed derivatization of carboxylic acids and phenols with pentafluorobenzyl bromide for electron capture gas chromatography, *Anal. Chem.*, 49, 832, 1977.
4. Avery, M.J. and Junk, G.A., Gas chromatography/mass spectrometry determination of water-soluble primary amines as their pentafluorobenzaldehyde imines, *Anal. Chem.*, 57, 790, 1985.

## Silylating Reagents

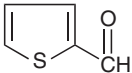
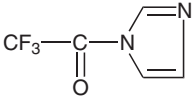
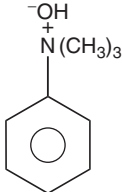
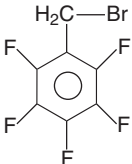
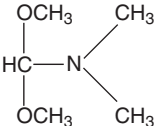
1. Metcalfe, L.D. and Martin, R.J., Gas chromatography of positional isomers of long chain amines and related compounds, *Anal. Chem.*, 44, 403, 1972.
2. Sen, H.P. and McGeer, P.L., Gas chromatography of phenolic and catecholic amines as the trimethylsilyl ethers, *Biochem. Biophys. Res. Commun.*, 13, 390, 1963.
3. Fogelgvist, E., Josefsson, B., and Roos, C., Determination of carboxylic acids and phenols in water by extractive alkylation using pentafluorobenzoylation, glass capillary g.c. and electron capture detection, HRC CC, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 3, 568, 1980.
4. Poole, C.F.C., Sye, W.F., Singhawangcha, S., Hsu, F., Zlatkis, A., Arfwidsson, A., and Vessman, J., New electron-capturing pentafluorophenyldialkylchlorosilanes as versatile derivatizing reagents for gas chromatography, *J. Chromatogr.*, 199, 123, 1980.
5. Quilliam, M.A., Ogilvie, K.K., Sadana, K.L., and Westmore, J.B., Study of rearrangement reactions occurring during gas chromatography of tert-butyl-dimethylsilyl ether derivatives of uridine, *J. Chromatogr.*, 194, 379, 1980.

6. Poole, C.F. and Zlatkis, A., Trialkylsilyl ether derivatives (other than TMS) for gas chromatography and mass spectrometry, *J. Chromatogr. Sci.*, 17, 115, 1979.
7. Francis, A.J., Morgan, E.D., and Poole, C.F., Flophemesyl derivatives of alcohols, phenols, amines and carboxylic acids and their use in gas chromatography with electron-capture detection, *J. Chromatogr.*, 161, 111, 1978.
8. Harvey, D.J., Comparison of fourteen substituted silyl derivatives for the characterization of alcohols, steroids and cannabinoids by combined gas-liquid chromatography and mass spectrometry, *J. Chromatogr.*, 147, 291, 1978.
9. Quilliam, M.A. and Yaraskavitch, J.M., Tertbutyldiphenylsilyl derivatization for liquid chromatography and mass spectrometry, *J. Liq. Chromatogr.*, 8, 449, 1985.

#### Derivatizing Reagents for Gas Chromatography

Derivatizing Reagent	Structure/Formula	Notes
<b>Acyating Reagents</b>		
Acetic anhydride	$(\text{CH}_3\text{CO})_2\text{O}$	Used for amino acids, steroids, urinary sugars, pesticides and herbicides, and narcotics
Chloroacetic anhydride	$(\text{CH}_2\text{ClCO})_2\text{O}$	Useful for electron capture detection of lower aliphatic primary amines
$\alpha$ , $p$ -Dibromoacetophenone	$\text{BrCH}_2-\text{C}(=\text{O})-$ 	Used for short- and medium-chain aliphatic carboxylic acids
Heptafluorobutyric anhydride	$(\text{CF}_3\text{CF}_2\text{CF}_2\text{CO})_2\text{O}$	Used in basic solution for alcohols, amines, nitrosamines, amino acids, and steroids; heptafluorobutylimidazole is used in a similar fashion in the analysis of phenols
Pentafluorobenzaldehyde		Useful for electron capture detection of several primary amines
Pentafluorobenzoyl chloride		Useful for electron capture detection of several primary amines
Pentafluoropropionic anhydride	$(\text{CF}_3\text{CF}_2\text{CO})_2\text{O}$	Used for aromatic monoamines and their metabolites
Propionic anhydride	$(\text{CH}_3\text{CH}_2\text{CO})_2\text{O}$	Used for amines, amino acids, narcotics

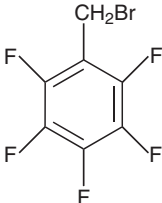
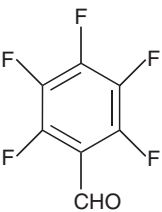
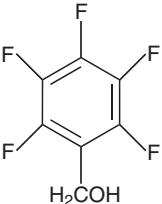
### Derivatizing Reagents for Gas Chromatography

Derivatizing Reagent	Structure/Formula	Notes
Pivalic anhydride	$[(\text{CH}_3)_3\text{CCO}]_2\text{O}$	Used for hormone analysis
2-Thiophene aldehyde		Used for electron capture detection of lower aliphatic primary amines
Trifluoroacetic anhydride	$(\text{CF}_3\text{CO})_2\text{O}$	Used for phenols, amines, amino acids, amino phosphoric acids, saccharides, and vitamins
<i>N</i> -Trifluoroacetylimidazole		Useful for the relatively straightforward acylation of hydroxyl groups, secondary or tertiary amines
Diazomethane	$\text{CH}_2=\text{N}=\text{N}$ + -	Used as a common alkylating agent; acts on acidic and enolic groups rapidly, and more slowly on other groups with replaceable hydrogens (the use of a Lewis acid catalyst such as $\text{BF}_3$ is sometimes helpful); all diazoalkanes are toxic and sometimes explosive, and are used in microscale operations only
Trimethylanilinium hydroxide (TMAH) (in methanol)		Useful for methylation of amines
Pentafluorobenzyl bromide		Useful for the derivatization of acids, amides, and phenols, providing great increase in sensitivity toward electron capture detection
<b>Esterification Reagents</b>		
Boron trifluoride + methanol	$\text{BF}_3 + \text{CH}_3\text{OH}$	Useful for carboxylic acids (aromatic and aliphatic), fatty acids, fatty acid esters, Krebs cycle acids
Boron trifluoride + <i>n</i> -propanol	$\text{BF}_3 + \text{CH}_3(\text{CH}_2)_2\text{OH}$	Useful for fatty acid, lactic acid, and succinic acid
<i>N,N</i> -Dimethyl formamide dimethyl acetal		Useful in the formation of fatty acid esters and for <i>N</i> -protected amino acids, sulfonamides, barbiturates
2-Bromopropane	$(\text{CH}_3)_2\text{CHBr}$	Used for amino acids and amides
1-Butanol	$\text{CH}_3(\text{CH}_2)_3\text{OH}$	Used for carboxylic acids and amino acids

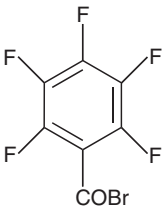
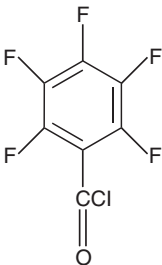
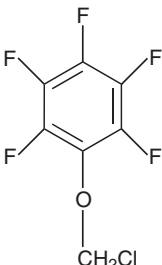
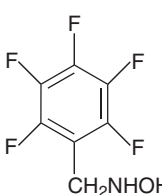
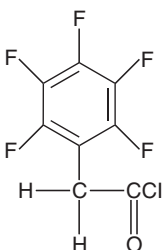
### Derivatizing Reagents for Gas Chromatography (continued)

Derivatizing Reagent	Structure/Formula	Notes
Hydrogen chloride + methanol	$\text{HCl} + \text{CH}_3\text{OH}$	Useful for carboxylic acids, branched-chain fatty acids, oxalic acid, amino acids, lipids; HCl serves as a catalytic agent
Sodium methoxide	$\text{CH}_3\text{ONa}$ in $\text{CH}_3\text{OH}$	Used for the transesterification of lipids
Sulfuric acid + methanol	$\text{H}_2\text{SO}_4 + \text{CH}_3\text{OH}$	Useful for carboxylic and fatty acids
Tetramethyl ammonium hydroxide	$(\text{CH}_3)_4\text{NOH}$ in $\text{CH}_3\text{OH}$	Useful for carboxylic acids, fatty acids, alkyd, and polyester resins
Thionyl chloride + alcohol	$\text{SOCl}_2$	Useful in the formation of esters of carboxylic acids and other acidic functional groups
2,2,2-Trichloroethanol	$\begin{array}{c} \text{H} \\   \\ \text{CCl}_3 - \text{C} - \text{OH} \\   \\ \text{H} \end{array}$	Useful in the esterification of short-chain acids followed by electron capture detection; sometimes used with trifluoroacetic anhydride in the presence of $\text{H}_2\text{SO}_4$
Triethyl orthoformate	$\text{HC}(\text{OC}_2\text{H}_5)_3$	Used for aminophosphoric acids
Trimethylphenyl-ammonium hydroxide	$(\text{CH}_3)_3\text{N}^+ - \text{C}_6\text{H}_5 - \text{OH}^-$ in $\text{CH}_3\text{OH}$	Used for fatty acids, aromatic acids, herbicides, pesticides

### Pentafluorophenyl Reagents

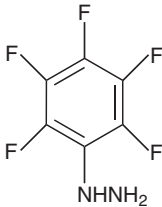
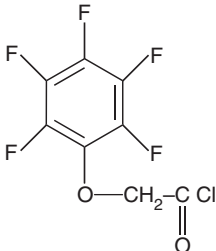
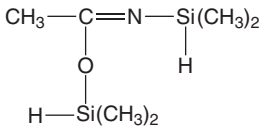
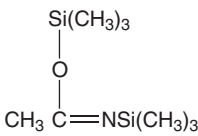
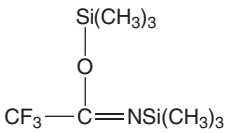
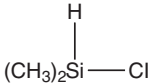
$\alpha$ -Bromopentafluorotoluene		Used to etherify sterols and phenols, in diethyl ether with the presence of potassium <i>t</i> -butoxide
Pentafluorobenzaldehyde		Used in derivatizing primary amines; greatly enhances electron capture detector response (to the picogram level)
Pentafluorobenzyl alcohol		Used in derivatizing carboxylic acids in acidic medium

### Derivatizing Reagents for Gas Chromatography (continued)

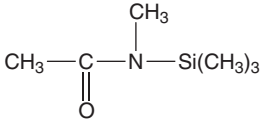
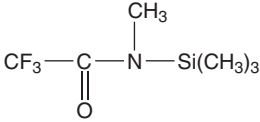
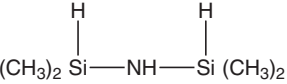
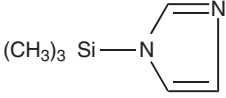
Derivatizing Reagent	Structure/Formula	Notes
Pentafluorobenzyl bromide	 <chem>Fc1cc(F)c(F)c(F)c1C(=O)Br</chem>	Used in the derivatization of carboxylic acids, phenols, mercaptans, and sulfamides; lachrymator; potentially unstable; high sensitivity for electron capture detection; not usable for formic acid
Pentafluorobenzyl chloride	 <chem>Fc1cc(F)c(F)c(F)c1C(=O)Cl</chem>	Used in the derivatization of amines, phenols, and alcohols; used in a solution of NaOH
Pentafluorobenzyl chloroformate	 <chem>Fc1cc(F)c(F)c(F)c1OCC(=O)Cl</chem>	Used in the derivatization of tertiary amines
Pentafluorobenzyl hydroxylamine	 <chem>Fc1cc(F)c(F)c(F)c1CNHO</chem>	Used in derivatization of ketones; can form both syn- and anti-isomers (two peaks)
Pentafluorophenacetyl chloride	 <chem>Fc1cc(F)c(F)c(F)c1CC(=O)Cl</chem>	Used in derivatization of alcohols, phenols, and amines



### Derivatizing Reagents for Gas Chromatography (continued)

Derivatizing Reagent	Structure/Formula	Notes
Pentafluorophenyl-hydrazine		Used in derivatization of ketones; can form both syn- and anti-isomers, resulting in two peaks
Pentafluorophenoxy-acetyl chloride		Used in derivatization of alcohols, phenols, and amines
<b>Silylating Reagents</b>		
Bis(dimethylsilyl)-acetamide (BSDA)		Similar in use and application to DMCS (see below)
<i>N,N</i> -Bis(trimethyl-silyl)-acetamide (BSA)		More reactive than HMDS (see below) or TMCS, but forming essentially similar derivatives; useful for alcohols, amines, amino acids, carboxylic acids, penicillic acid, purine and pyrimidine bases
Bis(trimethylsilyl)trifluoroacetamide (BSTFA)		Similar in use and application to BSA, but the derivatives are more volatile; by-products often elute with the solvent front; reacts more strongly than HMDS or TMCS; may promote enol-TMS formation unless ketone groups are protected
Dimethylchlorosilane (DMCS)		Similar in use and application to TMCS and HMDS, but usually forming more volatile and less thermally stable derivatives; also finds use in surface deactivation of chromatographic columns and injectors

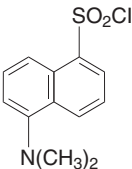
### Derivatizing Reagents for Gas Chromatography (continued)

Derivatizing Reagent	Structure/Formula	Notes
1,1,1,3,3,3-Hexamethyl disilazane (HMDS)	$(\text{CH}_3)_3\text{Si}-\text{NH}-\text{Si}(\text{CH}_3)_3$	Useful for such compounds as sugars, phenols, alcohols, amines, thiols, steroids; especially recommended for citric acid cycle compounds and amino acids; reaction is often carried out in pyridine or dimethyl formamide (the latter being preferred for 17-keto steroids); care must be taken to eliminate moisture; lowest silyl donating strength of all common silylating reagents
1,1,1,3,3,3-Hexamethyl disiloxane (HMDSO)	$(\text{CH}_3)_3\text{Si}-\text{O}-\text{Si}(\text{CH}_3)_3$	Similar in use and application to HMDS (see above)
<i>N</i> -Methyl- <i>N</i> -(trimethylsilyl)-acetamide (MSTA)		Similar in use and application to HMDS, but somewhat higher silyl donating strength
<i>N</i> -Methyl- <i>N</i> -(trimethylsilyl)trifluoroacetamide (MSTFA)		Similar to MSTFA, but produces the most volatile derivatives of all common silylating agents; particularly useful with low-molecular-mass derivatives
Tetramethyldisilazane (TMDS)		Similar in use and application to DMCS
<i>N</i> -Trimethylsilyl diethylamine (TMSDEA)	$(\text{CH}_3)_3\text{Si}-\text{N}(\text{C}_2\text{H}_5)_2$	Similar in use and application to DMCS
<i>N</i> -Trimethylsilyl imidazole (TMSIM)		Generally useful reagent with a high silyl donor ability; will not react with amino groups; will not cause formation of enol-ether on unprotected ketone groups; especially useful for ecdysones, norepinephrine, dopamine, steroids, sugars, sugar phosphates, and ketose isomers
Trimethylchlorosilane (TMCS)	$(\text{CH}_3)_3\text{SiCl}$	Similar properties and applications as for HMDS; useful for amino acid analyses; provides good response for electron capture detection; has relatively low silyl donating ability and is usually used in the presence of a base such as pyridine; may cause enol-ether formation with unprotected ketone groups; often used as a catalyst with other silylating reagents

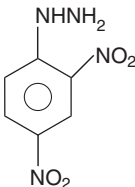
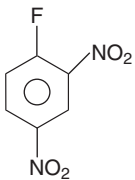
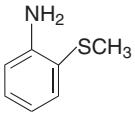
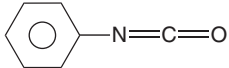
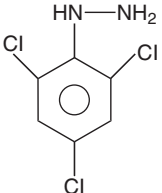
### Derivatizing Reagents for Gas Chromatography (continued)

Derivatizing Reagent	Structure/Formula	Notes
Halomethylflophe mesyl reagents	$\begin{array}{c} \text{CH}_3 \\   \\ \text{C}_6\text{F}_5-\text{Si}-\text{Y} \\   \\ \text{R} \end{array}$ $\text{R} = \text{CH}_2\text{Cl}$ $\text{Y} = \text{Cl}$	Similar in use and applications to the flophe mesyl and alkylflophe mesyl reagents
Halomethyldimethyl silyl reagents	$\begin{array}{c} \text{CH}_3 \\   \\ \text{XCH}_2-\text{Si}-\text{Y} \\   \\ \text{CH}_3 \end{array}$ $\text{X} = \text{Cl, Br, I}$ $\text{Y} = \text{Cl, N(C}_2\text{H}_5)_2, \text{NHSi(CH}_3)_2\text{CH}_2\text{X}$	Family of derivatizing agents that improve sensitivity of analyte to the electron capture detector; the response enhancement is in the order expected: $\text{I} > \text{Br} > \text{Cl} \gg \text{F}$ , reverse order of the volatility of these compounds; the iodomethyl-dimethylsilyl reagents are unstable, and these derivatives are usually prepared <i>in situ</i>
Flophe mesyl reagents	$\begin{array}{c} \text{CH}_3 \\   \\ \text{C}_6\text{F}_5-\text{Si}-\text{Y} \\   \\ \text{R} \end{array}$ $\text{R} = \text{CH}_3$ $\text{Y} = \text{Cl, NH}_2, \text{N(C}_2\text{H}_5)_2$	Family of reagents forming derivatives that have stabilities similar to those produced by TMSIM, BSA, MSTFA, and BSTFA, with additional electron capture detection sensitivity enhancement; usually used in pyridine as a solvent; reactions subject to steric considerations
Alkylflophe mesyl reagents	$\begin{array}{c} \text{CH}_3 \\   \\ \text{C}_6\text{F}_5-\text{Si}-\text{Y} \\   \\ \text{R} \end{array}$ $\text{R} = \text{CH(CH}_3)_2, \text{C(CH}_3)_3$ $\text{Y} = \text{Cl}$	Family of reagents forming derivatives of somewhat higher stability than the flophe mesyl reagents; reactions subject to steric considerations

### Miscellaneous Reagents

Boronation reagents	$(\text{OH})_2\text{B}-\text{R}$ $\text{R} = \text{CH}_3, -\text{C(CH}_3)_3,$ $\text{R}_2-\text{CH}_3$	Used to block two vicinal hydroxy groups; derivatives have very distinctive mass spectra that are easily identified
Carbon disulfide	$\text{CS}_2$	Used to derivatize primary amines to yield isothiocyanates
Dansyl chloride		Used for derivatization of tripeptides; provides high sensitivity toward spectrofluorimetric detection
Dimethyldiacetoxy-silane	$(\text{CH}_3)_2\text{Si}(\text{OOCCH}_3)_2$	Used in similar applications as the boronation reagents in pyridene or trimethylamine solvent

### Derivatizing Reagents for Gas Chromatography (continued)

Derivatizing Reagent	Structure/Formula	Notes
2,4-Dinitrophenylhydrazine		Useful in derivatizing carbonyl compounds and also provides a spot test for these compounds
1-Fluoro-2,4-dinitrofluorobenzene		Useful for derivatizing C <sub>1</sub> –C <sub>4</sub> primary and secondary amines, providing high electron capture detector response; this reagent is also useful for primary alicyclic amines
Girard reagent T	$(\text{CH}_3)_3\text{N}^+ - \text{Cl}^- - \text{CH}_2 - \text{C}(=\text{O})\text{NHNH}_2$	Useful for derivatization of saturated aldehydes
Hydrazine	NH <sub>2</sub> NH <sub>2</sub>	Used for the analysis of C-terminal peptide residue species
Methyl iodide + silver oxide	CH <sub>3</sub> I + Ag <sub>2</sub> O (in dimethylformamide)	Used to convert polyhydroxy compounds to the methyl ethers
Methyloxamine hydrochloride	CH <sub>3</sub> –O–NH·HCl	Used in derivatization of steroids and carbohydrates
2-Methylthioaniline		Used to form sulfur-bearing derivatives of benzaldehydes
Phenyl isocyanate		Used for derivatization of N-terminal peptide residue
2,4,6-Trichlorophenylhydrazine		Used for derivatization of carbonyl compounds

## DETECTORS FOR GAS CHROMATOGRAPHY

The following table provides some comparative data for the selection and operation of the more common detectors applied to capillary and packed column gas chromatography.<sup>1-7</sup>

### REFERENCES

1. Hill, H.H. and McMinn, D., Eds., *Detectors for Capillary Chromatography*, Wiley Interscience, John Wiley & Sons, 1992.
2. Buffington, R. and Wilson, M.K., *Detectors for Gas Chromatography: A Practical Primer*, Hewlett Packard Corp., Avondale, PA, 1987.
3. Buffington, R., *GC-Atomic Emission Spectroscopy Using Microwave Plasmas*, Hewlett Packard Corp., Avondale, PA, 1988.
4. Liebrand, R.J., Ed., *Basics of GC/IRD and GC/IRD/MS*, Hewlett Packard Corp., Avondale, PA, 1993.
5. Bruno, T.J., A review of hyphenated chromatographic instrumentation, *Sep. Purif. Methods*, 29, 63, 2000.
6. Bruno, T.J., A review of capillary and packed column chromatographs, *Sep. Purif. Methods*, 29, 27, 2000.
7. Sevcik, J., *Detectors in Gas Chromatography*, *Journal of Chromatography Library*, Vol. 4, Elsevier, Amsterdam, 1976.

### Detectors for Gas Chromatography

Detector	Limit of Detection	Linearity	Selectivity	Comments
Thermal conductivity detector (TCD), katharometer	$1 \times 10^{-10}$ g of propane (in helium carrier gas)	$1 \times 10^6$	Universal response, concentration detector	<ul style="list-style-type: none"> <li>• Ultimate sensitivity depends on analyte thermal conductivity difference with carrier gas</li> <li>• Since thermal conductivity is temperature dependent, response depends on cell temperature</li> <li>• Wire selection depends on chemical nature of analyte</li> <li>• Helium is recommended as carrier and makeup gas</li> </ul>
Gas density balance detector (GADE)	$1 \times 10^{-9}$ g of $H_2$ with $SF_6$ as carrier gas	$1 \times 10^6$	Universal response, concentration detector	<ul style="list-style-type: none"> <li>• Response and sensitivity is based on difference between relative molecular mass of analyte and that of the carrier gas; approximate calibration can be done on the basis of relative density</li> <li>• The sensing elements (hot wires) never touch sample, thus making GADE suitable for the analysis of corrosive analytes such as acid gases; gold-sheathed tungsten wires are most common</li> <li>• Best used with <math>SF_6</math> as a carrier gas, switched with nitrogen when analyses are required</li> <li>• Detector can be sensitive to vibrations and should be isolated on a cushioned base</li> </ul>
Flame ionization detector (FID)	$1 \times 10^{-11}$ to $1 \times 10^{-10}$ g	$1 \times 10^{-7}$	Organic compounds with C–H bonds	<ul style="list-style-type: none"> <li>• Ultimate sensitivity depends on the number of C–H bonds on analyte</li> <li>• Nitrogen is recommended as carrier gas and makeup gas to enhance sensitivity</li> <li>• Sensitivity depends on carrier, makeup, and jet gas flow rates</li> <li>• Column must be positioned 1–2 mm below the base of the flame tip</li> <li>• Jet gases must be of high purity</li> </ul>
Nitrogen–phosphorus detector (NPD), thermionic detector, alkali flame ionization detector	$4 \times 10^{-13}$ to $1 \times 10^{-11}$ g of nitrogen compounds $1 \times 10^{-13}$ to $1 \times 10^{-12}$ g of phosphorus compounds	$1 \times 10^{-4}$	$10^5$ to $10^6$ by mass selectivity of N or P over carbon	<ul style="list-style-type: none"> <li>• Does not respond to inorganic nitrogen such as <math>N_2</math> or <math>NH_3</math></li> <li>• Jet gas flow rates are critical to optimization</li> <li>• Response is temperature dependent</li> <li>• Used for trace analysis only and is very sensitive to contamination</li> <li>• Avoid use of phosphate detergents or leak detectors</li> <li>• Avoid tobacco use nearby</li> <li>• Solvent quenching is often a problem</li> </ul>

### Detectors for Gas Chromatography (continued)

Detector	Limit of Detection	Linearity	Selectivity	Comments
Electron capture detector (ECD)	$5 \times 10^{-14}$ to $1 \times 10^{-12}$ g	$1 \times 10^4$	Selective for compounds with high electron affinity, such as chlorinated organics; concentration detector	<ul style="list-style-type: none"> <li>Sensitivity depends on number of halogen atoms on analyte</li> <li>Used with nitrogen or argon/methane (95/5, mass/mass) carrier and makeup gases</li> <li>Carrier and makeup gases must be pure and dry</li> <li>The radioactive <math>^{63}\text{Ni}</math> source is subject to regulation and periodic inspection</li> </ul>
Flame photometric detector (FPD)	$2 \times 10^{-11}$ g of sulfur compounds $9 \times 10^{-13}$ g of phosphorus compounds	$1 \times 10^3$ for sulfur compounds $1 \times 10^4$ for phosphorus compounds	$10^5$ to 1 by mass selectivity of S or P over carbon	<ul style="list-style-type: none"> <li>Hydrocarbon quenching can result from high levels of <math>\text{CO}_2</math> in the flame</li> <li>Self-quenching of S and P analytes can occur with large samples</li> <li>Gas flows are critical to optimization</li> <li>Response is temperature dependent</li> <li>Condensed water can be a source of window fogging and corrosion</li> </ul>
Photoionization detector (PID)	$1 \times 10^{-12}$ to $1 \times 10^{-11}$ g	$1 \times 10^7$	Depends on ionization potential of analytes	<ul style="list-style-type: none"> <li>Used with lamps with energies of 10.0–10.2 eV</li> <li>Detector will have response to ionizable compounds such as aromatics and unsaturated organics, some carboxylic acids, aldehydes, esters, ketones, silanes, iodo- and bromoalkanes, alkylamines and amides, and some thiocyanates</li> </ul>
Sulfur chemiluminescence detector (SCD)	$1 \times 10^{-12}$ g of sulfur in sulfur compounds	$1 \times 10^4$	$10^7$ by mass selectivity of S over carbon	<ul style="list-style-type: none"> <li>Equimolar response to all sulfur compounds to within <math>\pm 10\%</math></li> <li>Requires pure hydrogen and oxygen combustion gases</li> <li>Instrument generates ozone <i>in situ</i>, which must be catalytically destroyed at detector outlet</li> <li>Catalyst operates at 950–975°C</li> <li>Detector operated at reduced pressure (<math>10^3\text{Pa}</math>)</li> </ul>
Electrolytic conductivity detector (ECD, Hall detector)	$10 \times 10^{-13}$ to $1 \times 10^{-12}$ g of chlorinated compounds $2 \times 10^{-12}$ g of sulfur compounds $4 \times 10^{-12}$ g of nitrogen compounds	$1 \times 10^6$ for chlorinated compounds $10^4$ for sulfur and nitrogen compounds	$10^6$ by mass selectivity of Cl over carbon $10^5$ to $10^6$ by mass selectivity of S and N over carbon	<ul style="list-style-type: none"> <li>Only high-purity solvents should be used</li> <li>Carbon particles in conductivity chamber can be problematic</li> <li>Frequent cleaning and maintenance is required</li> <li>Often used in conjunction with a photoionization detector</li> <li>For chlorine, use hydrogen as the reactant gas and <i>n</i>-propanol as the electrolyte</li> </ul>

Ion mobility detector (IMD)	$1 \times 10^{-12}$ g	$1 \times 10^3$ to $1 \times 10^4$	$10^3$	<ul style="list-style-type: none"> <li>For nitrogen or sulfur, hydrogen or oxygen can be used as reactant gas, and water or methanol as the electrolyte</li> <li>Ultra-high-purity reactant gases are required</li> <li>Amenable to use in handheld instruments; linear dynamic range of <math>10^3</math> for radioactive sources and <math>10^5</math> for photoionization sources</li> <li>Selectivity depends on mobility differences of ions</li> <li>Has been used for a wide variety of compounds, including amino acids, halogenated organics, explosives</li> </ul>
Mass selective detector (MSD), mass spectrometer (MS)	$1 \times 10^{-11}$ g (single-ion monitoring) $1 \times 10^{-8}$ g (scan mode)	$1 \times 10^5$	Universal	<ul style="list-style-type: none"> <li>Quadrupole and magnetic sector instruments available</li> <li>Must operate under moderate vacuum (<math>1 \times 10^{-4}</math> Pa)</li> <li>Requires a molecular jet separator to operate with packed columns</li> <li>Amenable to library searching for qualitative identification</li> <li>Requires tuning of electronic optics over the entire m/e range of interest</li> <li>See tables for mass spectrometry for structure elucidation and identification</li> </ul>
Infrared detector (IRD)	$1 \times 10^{-9}$ g of a strong infrared absorber	$1 \times 10^3$	Universal for compounds with mid-infrared active functionality	<ul style="list-style-type: none"> <li>A costly and temperamental instrument that requires high-purity carrier gas, a nitrogen purge of optical components (purified air will, in general, not be adequate)</li> <li>Must be isolated from vibrations</li> <li>Presence of carbon dioxide is a typical impurity band at <math>2200\text{--}2300\text{ cm}^{-1}</math></li> <li>Requires frequent cleaning and optics maintenance</li> <li>Amenable to library searching for qualitative identification</li> <li>See tables for infrared functionalities for structure elucidation and identification</li> </ul>
Atomic emission detector (AED)	$1 \times 10^{-13}$ to $2 \times 10^{-11}$ g of each element	$1 \times 10^3$ to $1 \times 10^4$	$10^3$ to $10^5$ , element to element	<ul style="list-style-type: none"> <li>Requires the use of ultra-high-purity carrier and plasma gases</li> <li>Plasma produced in a microwave cavity operated at 2450 MHz</li> <li>Scavenger gases (<math>\text{H}_2</math>, <math>\text{O}_2</math>) are used as dopants</li> <li>Photodiode array is used to detect emitted radiation</li> </ul>



## RECOMMENDED OPERATING RANGES FOR HOT WIRE THERMAL CONDUCTIVITY DETECTORS

The following table provides guidance in the operation of hot wire thermal conductivity detectors. The operating ranges are provided in mA dc for detector cells operated between 25 and 200°C.<sup>1</sup> The current ranges and the cold resistances provided are for typical wire lengths and configurations.

### REFERENCES

1. Gow-Mac Instrument Company Manual SB-13, *Thermal Conductivity Detector Elements for Gas Analysis*, Bethlehem, PA, 1995.

Carrier Gas					
Substance	H <sub>2</sub> , mA-dc	He, mA-dc	N <sub>2</sub> , mA-dc	CO <sub>2</sub> , Ar, mA-dc	Cold Resistance, Ohms, 25°C
Tungsten, W	250–500	250–400	100–175	90–130	18
Tungsten–rhenium, WX (97–3%)	250–400	230–375	100–150	90–130	26–32
Nickel, Ni (99.8%)	300–500	300–450	125–150	100–130	12.5
Gold-sheathed tungsten, AuW	250–400	250–375	100–150	75–120	24

## CHEMICAL COMPATIBILITY OF THERMAL CONDUCTIVITY DETECTOR WIRES

The following table provides guidance in the selection of hot wires for use in thermal conductivity detectors (TCDs).<sup>1-3</sup> This information is applicable to the operation of packed and open tubular columns. Some of the entries in this table deal with analytes, and others deal with solutions that might be used to clean the TCD cell.

### REFERENCES

1. Gow-Mac Instrument Company Manual SB-13, *Thermal Conductivity Detector Elements for Gas Analysis*, Bethlehem, PA, 1995.
2. Seveik, J., *Detectors in Gas Chromatography*, Elsevier Scientific Publishing Co., Amsterdam, 1976.
3. Lawson, A.E. and Miller, J.M., Thermal conductivity detectors in gas chromatography, *J. Gas Chromatogr.*, 4, 273, 1966.

**Chemical Compatibility of Thermal Conductivity Detector Wires**

Substance	Tungsten (W)	Rhenium– Tungsten (WX)	Nickel (Ni)	Gold-sheathed Tungsten (AuW)
Air/oxygen	Good	Good	Good	Very good
Water	Good	Good	Good	Good
Steam	Good below 700°C	Good below 700°C	Good	Good
Ammonia/amines	Good	Good	Poor in presence of water	Poor <sup>a</sup>
Carbon monoxide/carbon dioxide	Good	Good	Good	Good
Hydrogen	Good	Good	Good	Good
Nitrogen	Good	Good	Good	Fair
Fluorine	Poor (fluoride) forms at 20°C	Poor (fluoride) forms at 20°C	Good	Poor
Chlorine	Fair	Fair	Good	Fair
Bromine	Fair	Fair	Good	Fair
Iodine	Fair	Fair	Good	Fair
Sulfur	Fair	Good	Poor	Good
Hydrogensulfide/sulfur dioxide (sulfuric acid)	Fair	Fair	Poor	Good
Hydrogen chloride	Fair	Fair	Good	Fair
Aqua regia	Fair	Fair	Poor	Poor
Hydrogen fluoride	Fair	Fair	Good	Fair
Hydrogen fluoride/nitric acid	Poor	Poor	Good	Poor

<sup>a</sup> Gold-sheathed tungsten filaments are attacked by amines, but the process is somewhat reversible. The baseline departure will recover, but the peak will develop a significant tail.

## DATA FOR THE OPERATION OF GAS DENSITY DETECTORS

The following data provide useful guidance in the operation and optimization of procedures with the gas density balance detector in gas chromatography.<sup>1</sup> The property values were calculated with REFPROP.<sup>2</sup>

### REFERENCES

1. Nerheim, A.G., A gas density detector for gas chromatography, *Anal. Chem.*, 35, 1640, 1963.
2. Lemmon, E.W., McLinden, M.O., and Huber, M.L., *NIST Standard Reference Database 23: Reference Fluid Thermodynamic and Transport Properties-REFPROP*, Version 7.0, National Institute of Standards and Technology, Standard Reference Data Program, Gaithersburg, MD, 2002.

Data for the Operation of Gas Density Detectors			
Temperature, °C	Density, g/L	Cp/Cv	Viscosity μPa-s
<b>Argon, Ar, 24 psia</b>			
30	2.6251	1.6712	22.887
60	2.3877	1.6703	24.735
90	2.1899	1.6697	26.521
120	2.0224	1.6692	28.249
150	1.8787	1.6688	29.925
<b>Carbon Dioxide, CO<sub>2</sub>, 24 psia</b>			
30	2.9120	1.2950	15.179
60	2.6441	1.2802	16.614
90	2.4221	1.2679	18.018
120	2.2350	1.2576	19.391
150	2.0749	1.2487	20.731
<b>Helium, He, 24 psia</b>			
30	0.26258	1.6665	20.075
60	0.23895	1.6665	21.417
90	0.21923	1.6665	22.726
120	0.20251	1.6665	24.006
150	0.18816	1.6665	25.259
<b>Hydrogen, H<sub>2</sub>, 24 psia</b>			
30	0.13222	1.4047	9.0188
60	0.12032	1.4015	9.6186
90	0.11039	1.3997	10.200
120	0.10197	1.3987	10.766
150	0.094745	1.3982	11.317
<b>Nitrogen, N<sub>2</sub>, 24 psia</b>			
30	1.8396	1.4022	18.052
60	1.6734	1.4013	19.399
90	1.5348	1.4002	20.695
120	1.4175	1.3989	21.945
150	1.3169	1.3973	23.153

**Data for the Operation of Gas Density  
Detectors (continued)**

Temperature, °C	Density, g/L	Cp/Cv	Viscosity μPa-s
<b>Sulfur Hexafluoride, SF<sub>6</sub>, 24 psia</b>			
30	9.7615	1.0997	15.646
60	8.8401	1.0913	17.105
90	8.0832	1.0851	18.514
120	7.4489	1.0804	9.869
150	6.9090	1.0768	21.177
<b>1,1,1,2-Tetrafluoroethane, R134a, CF<sub>3</sub>CFH<sub>2</sub>, 24 psia</b>			
30	6.9186	1.1247	12.013
60	6.2347	1.1116	13.209
90	5.6842	1.1021	14.365
120	5.2285	1.0949	15.486
150	4.8436	1.0890	16.575

## PHASE RATIO FOR CAPILLARY COLUMNS

The phase ratio is an important parameter used in the design of capillary (open tubular) column separations.<sup>1</sup> This quantity relates the partition coefficient ( $K$ ) to the partition ratio ( $k$ ):

$$K = k\beta$$

where  $\beta$  is the phase ratio, defined as the ratio of the volume occupied by the gas or mobile phase ( $V_m$ ) relative to that occupied by the liquid or stationary phase ( $V_s$ ). For wall-coated open tubular columns, the phase ratio can be found from

$$\beta = r/2d_f$$

where  $r$  is the internal radius of the column and  $d_f$  is the thickness of the stationary phase film. The following table provides the phase ratio for common combinations of column internal diameter and stationary phase film thickness. These values are given to the nearest whole number, since only an approximate value is needed for most analytical applications.

## REFERENCES

1. Sandra, P., *High Resolution Gas Chromatography*, Hewlett Packard Corp., Avondale, PA, 1989.

**Phase Ratio for Capillary Columns**

Film Thickness, $\mu\text{m}$	Column Inside Diameter, mm							
	0.05	0.10	0.20	0.30	0.32	0.40	0.50	0.53
0.03	417	833	1667	2500	2667	3333	4167	4417
0.06	208	417	833	1250	1333	1667	2083	2208
0.1	125	250	500	750	800	1000	1250	1325
0.2	63	125	250	375	400	500	625	663
0.3	42	83	167	250	267	333	417	442
0.4	31	63	125	188	200	250	313	331
0.5	25	50	100	150	160	200	250	265
0.6	21	42	83	125	133	167	208	221
0.7	18	36	71	107	114	143	179	189
0.8	16	31	63	94	100	125	156	166
0.9	14	28	56	83	89	111	139	147
1.0	13	25	50	75	80	100	125	133
1.5	8	17	34	50	53	67	83	88
2.0	6.3	13	25	38	40	50	63	66
2.5	5	10	20	30	34	40	50	53
3.0	4	8	17	25	27	33	42	44
3.5	4	7	14	21	23	29	18	38
4.0	3	6	13	19	20	25	32	33
4.5	3	6	11	17	18	22	29	29
5.0	2.5	5	10	15	16	20	25	27
5.5	2	5	9	14	15	18	23	24
6.0	2	4	8	13	13	17	21	22
6.5	2	4	8	12	12	15	19	20
7.0	2	4	7	11	11	14	18	19
7.5	2	3	7	10	11	13	17	18
8.0	2	3	6	9	10	13	16	17
8.5	1	3	6	9	9	12	15	16
9.0	1	3	6	8	9	11	14	15

## MARTIN–JAMES COMPRESSIBILITY FACTOR AND GIDDINGS PLATE HEIGHT CORRECTION FACTOR

The following table provides the Martin–James compressibility factor,  $j$ ,<sup>1</sup> and the Giddings plate height correction factor,  $f$ ,<sup>2</sup> for chromatographically useful pressures. These quantities are defined as

$$j = 3/2 \left[ \frac{\left[ \left( P_i^{\text{abs}} / P_o \right)^2 - 1 \right]}{\left[ \left( P_i^{\text{abs}} / P_o \right)^3 - 1 \right]} \right]$$

$$f = 9/8 \left[ \frac{\left[ \left( P_i^{\text{abs}} / P_o \right)^4 - 1 \right] \left[ \left( P_i^{\text{abs}} / P_o \right)^2 - 1 \right]}{\left[ \left( P_i^{\text{abs}} / P_o \right)^3 - 1 \right]^2} \right]$$

where  $P_i$  is the absolute inlet pressure and  $P_o$  is the outlet pressure.

The inlet pressures listed in the table are gauge pressures; the pressures used in the calculations of  $j$  and  $f$  are absolute pressures. Thus, atmospheric pressure had already been accounted for in the inlet pressure. The outlet pressure is taken as standard atmospheric pressure. As an example, for a measured gauge pressure of 137.9 kPa (20 psig), the ratio  $P_i^{\text{abs}}/P_o$  is 2.361. The actual value of the atmospheric pressure will vary day to day, and with altitude; thus if an exact value for  $j$  or  $f$  is desired, local pressure measurements must be made.

## REFERENCES

1. Grob, R.L., *Modern Practice of Gas Chromatography*, 2nd ed., John Wiley & Sons (Wiley Interscience), New York, 1985.
2. Lee, M.L., Yang, F.J., and Bartle, K.D., *Open Tubular Column Gas Chromatography*, John Wiley & Sons (Wiley Interscience), New York, 1984.

**Martin–James Compressibility Factor  
and Giddings Plate Height Correction  
Factor**

Pressure	$j$	$f$
15.0	0.638	1.034
16.0	0.622	1.037
17.0	0.606	1.039
18.0	0.592	1.042
19.0	0.578	1.044
20.0	0.564	1.046
25.0	0.505	1.057
30.0	0.456	1.066
35.0	0.416	1.074
40.0	0.381	1.080
45.0	0.352	1.085
50.0	0.327	1.090
55.0	0.305	1.093
60.0	0.286	1.096

## CRYOGENS FOR SUBAMBIENT TEMPERATURE GAS CHROMATOGRAPHY

The following table lists properties of common cryogenic fluids used to produce subambient temperatures for gas chromatographic columns.<sup>1-5</sup> These properties are of value in designing low-temperature chromatographic experiments efficiently and safely. Due to the potential dangers in handling extremely low temperatures and high pressures, appropriate precautions must be observed. These precautions must include protective clothing and shielding to prevent frostbite. Most cryogenic fluids can create a health hazard if they are vaporized in an inhabited area. Even small quantities can contaminate and displace air in a relatively short period. It may be advisable to locate a self-contained breathing apparatus immediately outside the laboratory in which the cryogens are being used. The effect of low temperatures on construction materials (of GC ovens and columns, for example) should also be considered. In this respect, differential expansion and tensile strength changes are pertinent issues. A dew point vs. moisture content table is also provided to allow the user to estimate the effects of ambient and impure water. The viscosity data are provided in cP, which is equivalent to mPa·sec, the appropriate SI unit. The freezing points are reported at 0.101325 MPa (1 atm), and the expansion ratios are reported at STP.

If temperatures no lower than approximately  $-40^{\circ}\text{C}$  are required, the use of a Ranque–Hilsch vortex tube should be considered.<sup>6-8</sup> This device requires a source of clean, dry compressed air at a pressure of approximately 0.70 MPa (100 psi) for proper operation. The flow rate of air that is required depends on the volume of space to be cooled.

## REFERENCES

1. Zabetakis, M.G., *Safety with Cryogenic Fluids*, Plenum Press, New York, 1967.
2. Cook, G.A., Ed., *Argon, Helium and the Rare Gases*, John Wiley & Sons (Interscience) New York, 1961.
3. Brettell, T.A. and Grob, R.L., Cryogenic techniques in gas chromatography, *Am. Lab.*, 17, 19, 1985.
4. Cowper, C.J. and DeRose, A.J., *The Analysis of Gases by Chromatography*, Pergamon Press, Oxford, 1983.
5. *Matheson Gas Data Book*, 7th ed., The Matheson Company, East Rutherford, NJ, 2001.
6. Bruno, T.J., Vortex cooling for subambient temperature gas chromatography, *Anal. Chem.*, 58, 1596, 1986.
7. Bruno, T.J., Vortex refrigeration of HPLC components, *Liq. Chromatogr. HPLC Mag.*, 4, 134, 1986.
8. Bruno, T.J., Laboratory applications of the vortex tube, *J. Chem. Educ.*, 64, 987, 1987.

**Cryogenics for Subambient Temperature Gas Chromatography**

<b>Cryogen Name</b>	<b>Relative Molecular Mass</b>	<b>Freezing Point, °C (K)</b>	<b>Heat of Fusion, J/g</b>	<b>Normal Boiling Point, °C (K)</b>	<b>Heat of Vaporization, J/g</b>	<b>Critical Temperature, °C (K)</b>	<b>Critical Pressure, MPa</b>	<b>Critical Density, g/l</b>
Argon, Ar	39.948	−189.4 (83.8)	27.6	−185.9 (87.3)	163.2	−122.3 (150.9)	4.89	530.5
Carbon dioxide, CO <sub>2</sub>	44.01	−78.5 <sup>1</sup> (194.7)	198.7	−56.6 (216.6)	151.5	31.1 (304.2)	7.38	468
Helium, He	4.003	−272 <sup>b</sup> (1)	— <sup>b</sup>	−269.0 (4.2)	23.0 (15°C)	−268.0 (5.2)	0.23	69.3
Methane, CH <sub>4</sub>	16.04	−182.6 (90.6)	58.6	−161.5 (87.3)	510.0	−82.1 (190.1)	4.64	162.5
Nitrogen, N <sub>2</sub>	28.013	−210.1 (63.1)	25.5	−195.81 (77.3)	199.6	−146.9 (150.9)	3.4	311
Oxygen, O <sub>2</sub>	31.999	−218.8 (54.4)	13.8	−183.0 (90.2)	213.0	−118.4 (154.8)	5.04	410

<b>Cryogen Name</b>	<b>Vapor Pressure, MPa</b>	<b>Gas Density, g/l</b>	<b>Liquid/Gas Expansion Ratio</b>	<b>Heat Capacity C<sub>p</sub>, J/(kg·K)</b>	<b>Heat Capacity C<sub>v</sub>, J/(kg·K)</b>	<b>Thermal Conductivity × 10<sup>−2</sup> w/(m·K)</b>	<b>Viscosity Pa·sec × 10<sup>5</sup> (cP)</b>	<b>Solubility in Water, 0°C, v/v</b>
Argon, Ar	— <sup>a</sup>	1.63	860	523.8 (21°C)	313.8 (15.6°C)	1.44 (233 K)	2.21 (21°C)	0.056
Carbon dioxide, CO <sub>2</sub>	5.72 (21°C)	1.98	790	831.8 (15.6°C)	638.8 (15.6°C)	1.17 (233 K)	1.48 (21°C)	0.90
Helium, He	— <sup>a</sup>	0.16	780	5221.6 (21°C)	3146.4 (15.6°C)	12.76 (233 K)	1.96 (21°C)	0.0086
Methane, CH <sub>4</sub>	— <sup>a</sup>	0.7174	650	2205.4 (15.6°C)	1687.0 (15.6°C)	2.57 (233 K)	1.20 (21°C)	
Nitrogen, N <sub>2</sub>	— <sup>a</sup>	1.14	710	1030.6 (21°C)	738.6 (21°C)	2.11 (233 K)	1.744 (15°C)	0.023
Oxygen, O <sub>2</sub>	— <sup>a</sup>	1.3	875	910.9 (15°C)	650.2 (15°C)	2.11 (233 K)	2.06 (20°C)	0.0489

<sup>a</sup> Fluid is supercritical at ambient temperature.

<sup>b</sup> Helium will not solidify at 1 atmosphere pressure (0.101325 MPa). The approximate pressure at which solidification can occur is calculated to be 2535 kPa.



## DEW POINT–MOISTURE CONTENT

Dew Point, °F	Dew Point, °C	Moisture, ppm (v/v)
–130	–90.0	0.1
–120	–84.4	0.25
–110	–78.9	0.63
–105	–76.1	1.00
–104	–75.6	1.08
–103	–75.0	1.18
–102	–74.4	1.29
–101	–73.9	1.40
–100	–73.3	1.53
–99	–72.8	1.66
–98	–72.2	1.81
–97	–71.7	1.96
–96	–71.7	2.15
–95	–70.6	2.35
–94	–70.0	2.54
–93	–69.4	2.76
–92	–68.9	3.00
–91	–68.3	3.28
–90	–67.8	3.53
–89	–67.2	3.84
–88	–66.7	4.15
–87	–66.1	4.50
–86	–65.6	4.78
–85	–65.0	5.30
–84	–64.4	5.70
–83	–63.9	6.20
–82	–63.3	6.60
–81	–62.8	7.20
–80	–62.2	7.80
–79	–61.7	8.40
–78	–61.1	9.10
–77	–60.6	9.80
–76	–60	10.50
–75	–59.4	11.40
–74	–58.9	12.30
–73	–58.3	13.30
–72	–57.8	14.30
–71	–57.2	15.40
–70	–56.7	16.60
–69	–56.1	17.90
–68	–55.6	19.20
–67	–55.0	20.60
–66	–54.4	22.10
–65	–53.9	23.60
–64	–53.3	25.60
–63	–52.8	27.50
–62	–52.2	29.40
–61	–51.7	31.70
–60	–51.1	34.00

## CHAPTER 2

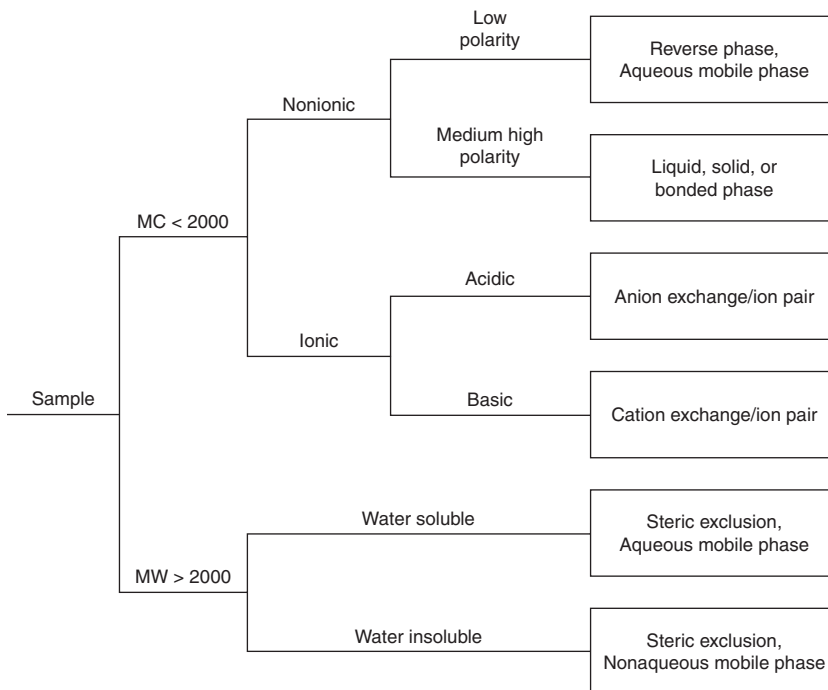
# High-Performance Liquid Chromatography

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## MODES OF LIQUID CHROMATOGRAPHY

The following flowchart provides a rough guide among the various liquid chromatographic techniques, based on sample properties.



Courtesy of Millipore Corporation, Waters Chromatography Division, Billerica, MA.

## SOLVENTS FOR LIQUID CHROMATOGRAPHY

The following table provides the important physical properties for the selection of solvent systems for high-performance liquid chromatography (HPLC).<sup>1-7</sup> These properties are required for proper detector selection, and the prediction of expected column pressure gradients. The values of the dielectric constant aid in estimating the relative solubilities of solutes and other solvents. Data on adsorption energies of useful HPLC solvents on silica and alumina (the eluotropic series) can be found in the chapter on thin-layer chromatography. Here we present the values for alumina,  $\epsilon^\circ$ , not because this is a common surface encountered in HPLC, but because there are more data on this surface than for silica. These numbers should be used for trend analysis. The data presented were measured at 20°C, unless otherwise indicated (in parentheses). The solubility parameters,  $\delta$ , defined fundamentally as the cohesive energy per unit volume, were calculated from vapor pressure data<sup>8</sup> or estimated from group contribution methods.<sup>9</sup> Those values obtained by group contribution are indicated by an asterisk.

## REFERENCES

1. Willard, H.H., Dean, J.A., Settle, F.A., and Merritt, L.L., *Instrumental Methods of Analysis*, 7th ed., Wadsworth Publishing Co., Belmont, CA, 1995.
2. Snyder, L.R. and Kirkland, J.J., *Introduction to Modern Liquid Chromatography*, 2nd ed., John Wiley & Sons (Interscience), New York, 1979.
3. Dreisbach, R.R., *Physical Properties of Chemical Compounds*, Number 22 of the Advances in Chemistry Series, American Chemical Society, Washington, D.C., 1959.
4. Krstulovic, A.M. and Brown, P.R., *Reverse Phase High Performance Liquid Chromatography*, John Wiley & Sons (Interscience), New York, 1982.
5. Lide, D.R., Ed., *CRC Handbook of Chemistry and Physics*, 83rd ed., CRC Press, Boca Raton, FL, 2002.
6. Poole, C.F. and Shuttles, S.A., *Contemporary Practice of Chromatography*, Elsevier, Amsterdam, 1984.
7. Braithwaite, A. and Smith, F.J., *Chromatographic Methods*, 4th ed., Chapman & Hall, London, 1985.
8. Hoy, K.L., New values of the solubility parameters from vapor pressure data, *J. Paint Technol.*, 42(541), 76, 1970.
9. Barton, A.F.M., *Handbook of Solubility Parameters and Other Cohesion Parameters*, 2nd ed., CRC Press, Boca Raton, FL, 1991.

# Solvents for Liquid Chromatography

Solvent	$\epsilon^\circ$	$\delta$	Viscosity, mPa·sec (20°C)	UV Cutoff, nm	Refractive Index (20°C)	Normal Boiling Point, °C	Dielectric Constant (20°C)
Acetic acid	1.0	13.01	1.31 (15)		1.372	117.9	6.2
Acetone	0.56	9.62	0.30 (25)	330	1.359	56.3	20.7 (25)
Acetonitrile	0.65	12.11	0.34 (25)	190	1.344	81.6	37.5
Benzene	0.32	9.16	0.65	278	1.501	80.1	2.284
1-Butanol		11.60	2.95	215	1.399	117.7	17.8
2-Butanol		11.08	4.21	260	1.397	99.6	15.8 (25)
<i>n</i> -Butyl acetate		8.69	0.73	254	1.394	126.1	
<i>n</i> -Butyl chloride		8.37	0.47 (15)	220	1.402	78.4	
Carbon tetrachloride	0.18	8.55	0.97	263	1.460	76.8	2.238
Chlorobenzene	0.30	9.67	0.80	287	1.525	131.7	2.708
Chloroform	0.40	9.16	0.58	245	1.446	61.2	4.806
Cyclohexane	0.04	8.19	0.98	200	1.426	80.7	2.023
Cyclopentane	0.05	8.10	0.44	200	1.406	49.3	1.965
<i>o</i> -Dichlorobenzene		10.04	1.32 (25)	295	1.551	180.5	9.93 (25)
<i>N,N</i> -Dimethylacetamide			2.14	268	1.438	166.1	37.8
Dimethylformamide		11.79	0.92	268	1.430	153.0	36.7
Dimethyl sulfoxide	0.62	12.8	2.20	286	1.478	189.0	4.7
1,4-Dioxane	0.56	10.13	1.44 (15)	215	1.422	101.3	2.209 (25)
2-Ethoxyethanol			2.05	210	1.408	135.6	
Ethyl acetate	0.58	8.91	0.46	256	1.372	77.1	6.02 (25)
Ethyl ether	0.38	7.53	0.24	218	1.352	34.6	4.335
Glyme (ethylene glycol dimethyl ether)			0.46 (25)	220	1.380	93.0	
<i>n</i> -Heptane	0.01	7.50	0.42	200	1.388	98.4	1.92
<i>n</i> -Hexadecane			3.34	200	1.434	287.0	
<i>n</i> -Hexane	0.01	7.27	0.31	200	1.375	68.7	1.890
Isobutyl alcohol		11.24	4.70 (15)	220	1.396	107.7	15.8 (25)
Methanol	0.95	14.50	0.55	205	1.328	64.7	32.63 (25)
2-Methoxyethanol		11.68	1.72	210	1.402	124.6	16.9
2-Methoxyethyl acetate				254	1.402	144.5	
Methylene chloride	0.42	9.88	0.45 (15)	233	1.424	39.8	9.08
Methylethylketone	0.51	9.45	0.42 (15)	329	1.379	79.6	18.5
Methylisoamylketone		8.65		330	1.406	−144.0	
Methylisobutylketone	0.43	8.58	0.54 (25)	334	1.396	116.5	
<i>N</i> -Methyl-2-pyrrolidone			1.67 (25)	285	1.488	202.0	32.0
<i>n</i> -Nonane		7.64	0.72	200	1.405	150.8	1.972
<i>n</i> -Pentane	0.00	7.02	0.24	200	1.357	36.1	1.84
Petroleum ether	0.01		0.30	226		30–60	
$\beta$ -Phenethylamine				285	1.529 (25)	197–198	
1-Propanol	0.82	12.18	2.26	210	1.386	97.2	20.1 (25)
2-Propanol	0.82	11.44	2.86 (15)	205	1.377	82.3	18.3 (25)
Propylene carbonate		13.3			1.419	240.0	
Pyridine	0.71	10.62	0.95	330	1.510	115.3	12.3 (25)
Tetrachloroethylene		9.3	0.93 (15)	295	1.506	121.2	
Tetrahydrofuran	0.45	9.1	0.55	212	1.407	66.0	7.6
Tetramethyl urea				265	1.449 (25)	175.2	23.0
Toluene	0.29	8.93	0.59	284	1.497	110.6	2.379 (25)
Trichloroethylene		9.16	0.57	273	1.477	87.2	3.4 (16)
1,1,2-Trichloro-1,2,2-trifluoroethane			0.71	231	1.356 (25)	47.6	
2,2,4-Trimethylpentane	0.01	6.86	0.50	215	1.391	99.2	1.94
Water	Large	23.53	1.00	<190	1.333	100.0	80.0
<i>o</i> -Xylene	0.26	9.06	0.81	288	1.505	144.4	2.568
<i>p</i> -Xylene				290	1.5004	138.5	2.270

## INSTABILITY OF HPLC SOLVENTS

Solvents that are commonly used in high-performance liquid chromatography frequently have inherent chemical instabilities that must be considered when designing an analysis, or in the interpretation of results.<sup>1,2</sup> In many cases, such solvents are obtainable with stabilizers added to control the instability or to slow the reaction. Reactive solvents that do not have stabilizers must be used quickly or be given proper treatment. In either case, it is important to understand that the solvents (as they may be used in an analysis) are not necessarily pure materials.

## REFERENCES

1. Sadek, P.C., *The HPLC Solvent Guide*, 2nd ed., Wiley Interscience, New York, 2002.
2. Bruno, T.J. and Straty, G.C., *J. Res. Natl. Bur. Stand. (U.S.)*, Thermophysical property measurement on chemically reacting systems — a case study, 91, 135, 1986.

Instability of HPLC Solvents		
Solvent	Contaminants, Reaction Products	Stabilizers
<b>Ethers</b>		
Diethyl ether	Peroxides <sup>a</sup>	2–3% (v/v) ethanol <sup>b</sup> 1–10 ppm (mass/mass) BHT (1.5–3.5% ethanol) + (0.2–0.5% water) + (5–10 ppm (mass/mass) BHT)
Isopropyl ether	Peroxides <sup>a</sup>	0.01% (mass/mass) hydroquinone 5–100 ppm (mass/mass) BHT
1,4-Dioxane	Peroxides <sup>a</sup>	25–1500 ppm (mass/mass) BHT
Tetrahydrofuran	Peroxides <sup>a</sup>	25–250 ppm (mass/mass) BHT
<b>Chlorinated Alkanes</b>		
Chloroform	Hydrochloric acid, chlorine, phosgene (Cl <sub>2</sub> CO)	0.5–1% (v/v) ethanol 50–150 ppm (mass/mass) amylene <sup>c</sup> Various ethanol amylene blends
Dichloromethane (methylene chloride)	Hydrochloric acid, chlorine, phosgene (Cl <sub>2</sub> CO)	25 ppm (mass/mass) amylene 25 ppm (mass/mass) cyclohexene 400–600 ppm (mass/mass) methanol Various amylene methanol blends
<b>Alcohols</b>		
Ethanol	Water; numerous denaturants are commonly added	
Methanol	Water; formaldehyde, acetals, hemiacetals (at elevated temperature)	
Acetone	Diacetone alcohol and higher oligomers	

*Note:* BHT = 2,6-di-*t*-butyl-*p*-cresol.

<sup>a</sup> The peroxide concentration that is usually considered hazardous is 250 ppm (mass/mass).

<sup>b</sup> Ethanol does not actually stabilize diethyl ether, and it is not a peroxide scavenger, although it was thought to be so in the past. It is still available in chromatographic solvents to preserve the utility of retention relationships and analytical methods.

<sup>c</sup> Amylene is a generic name for 2-methyl-2-butene.

## ULTRAVIOLET ABSORBANCE OF REVERSE PHASE MOBILE PHASES

The following table provides guidance in the selection of mobile phases that are to be used in conjunction with ultraviolet spectrophotometric detection.<sup>1,2</sup> The data in this table differ from the data in the other solvent tables in this volume in that the wavelength dependence of absorbance is provided here. Moreover, common mixed mobile phases are considered here. The percentages that are given are on the basis of v/v.

### REFERENCES

1. Snyder, L.R., Kirkland, J.J., and Glajch, J.L., *Practical HPLC Method Development*, John Wiley & Sons, New York, 1997.
2. Li, J.B., Signal to noise optimization in HPLC UV detection, *LC/GC*, 10, 856, 1992.

# Ultraviolet Absorbance of Reverse Phase Mobile Phases

	Absorbance (AU) at Wavelength (nm) Specified									
	200	205	210	215	220	230	240	250	260	280
<b>Solvents</b>										
Acetonitrile	0.05	0.03	0.02	0.01	0.01	<0.01				
Methanol	2.06	1.00	0.53	0.37	0.24	0.11	0.05	0.02	<0.01	
Degassed	1.91	0.76	0.35	0.21	0.15	0.06	0.02	<0.01		
Isopropanol	1.80	0.68	0.34	0.24	0.19	0.08	0.04	0.03	0.02	0.02
Tetrahydrofuran										
Fresh	2.44	2.57	2.31	1.80	1.54	0.94	0.42	0.21	0.09	0.05
Old <sup>a</sup>	>2.5	>2.5	>2.5	>2.5	>2.5	>2.5	>2.5	>2.5	2.5	1.45
<b>Acids and Bases</b>										
Acetic acid, 1%	2.61	2.63	2.61	2.43	2.17	0.87	0.14	0.01	<0.01	
Hydrochloric acid, 6 mM (0.02%)	0.11	0.02	<0.01							
Phosphoric acid, 0.1%	<0.01									
Trifluoroacetic acid										
0.1% in water	1.20	0.78	0.54	0.34	0.20	0.06	0.02	<0.01		
0.1% in acetonitrile	0.29	0.33	0.37	0.38	0.37	0.25	0.12	0.04	0.01	<0.01
Ammonium phosphate, dibasic, 50 mM	1.85	0.67	0.15	0.02	<0.01					
Triethylamine, 1%	2.33	2.42	2.50	2.45	2.37	1.96	0.50	0.12	0.04	<0.01
<b>Buffers and Salts</b>										
Ammonium acetate, 10 mM	1.88	0.94	0.53	0.29	0.15	0.02	<0.01			
Ammonium bicarbonate, 10 mM	0.41	0.10	0.01	<0.01						
EDTA (ethylenediamine tetraacetic acid), disodium, 1 mM	0.11	0.07	0.06	0.04	0.03	0.03	0.02	0.02	0.02	0.02
HEPES [N-(2-hydroxyethyl) piperazine- N'-2-ethanesulfonic acid], 10 mM, pH 7.6	2.45	2.50	2.37	2.08	1.50	0.29	0.03	<0.01		



MES [2-( <i>N</i> -morpholino ethanesulfonic acid], 10 mM, pH 6.0	2.42	2.38	1.89	0.90	0.45	0.06	<0.01			
Potassium phosphate Monobasic, 10 mM	0.03	<0.01								
Dibasic, 10 mM	0.53	0.16	0.05	0.01	<0.01					
Sodium acetate, 10 mM	1.85	0.96	0.52	0.30	0.15	0.03	<0.01			
Sodium chloride, 1 mM	2.00	1.67	0.40	0.10	<0.01					
Sodium citrate, 10 mM	2.48	2.84	2.31	2.02	1.49	0.54	0.12	0.03	0.02	0.01
Sodium formate, 10 mM	1.00	0.73	0.53	0.33	0.20	0.03	<0.01			
Sodium phosphate, 100 mM, pH 6.8	1.99	0.75	0.19	0.06	0.02	0.01	0.01	0.01	0.01	<0.01
Tris-hydrochloric acid, 20 mM										
pH 7.0	1.40	0.77	0.28	0.10	0.04	<0.01				
pH 8.0	1.80	1.90	1.11	0.43	0.13	<0.01				

<sup>a</sup> For additional information, see the table in the "Instability of HPLC Solvents" section in this chapter.

From Snyder, L.R., Kirkland, J.J., and Glajch, J.L., *Practical HPLC Method Development*, 2nd ed., John Wiley & Sons, New York, 1997. With permission.

## ULTRAVIOLET ABSORBANCE OF NORMAL PHASE MOBILE PHASES

The following table provides guidance in the selection of mobile phases that are to be used in conjunction with ultraviolet spectrophotometric detection.<sup>1</sup>

### REFERENCES

1. Snyder, L.R., Kirkland, J.J., and Glajch, J.L., *Practical HPLC Method Development*, John Wiley & Sons, New York, 1997.

Ultraviolet Absorbance of Normal Phase Mobile Phases							
Solvent	Absorbance (A) at Wavelength (nm) Indicated						
	200	210	220	230	240	250	260
Ethyl acetate	>1.0	>1.0	>1.0	>1.0	>1.0	>1.0	0.10
Ethyl ether	>1.0	>1.0	0.46	0.27	0.18	0.10	0.05
Hexane	0.54	0.20	0.07	0.03	0.02	0.01	0.00
Dichloromethane	>1.0	>1.0	>1.0	1.4	0.09	0.00	0.00
Methyl- <i>t</i> -butyl ether	>1.0	0.69	0.54	0.45	0.26	0.11	0.05
<i>n</i> -Propanol	>1.0	0.65	0.35	0.15	0.07	0.03	0.01
<i>i</i> -Propanol	>1.0	0.44	0.20	0.11	0.05	0.03	0.02
Tetrahydrofuran	>1.0	>1.0	0.70	0.50	0.30	0.16	0.09

## SOME USEFUL ION-PAIRING AGENTS

The following table provides a short list of ion pair chromatographic modifiers, for use in the separation ionic or ionizable species.<sup>1-4</sup> The use of these modifiers can often greatly improve the chromatographic performance of both normal and reverse phase systems. In many cases, new column technology has superseded the use of ion-pairing agents, especially when mass spectrometry is used with HPLC. Ion-pairing agents can cause numerous difficulties when the column is interfaced with a mass spectrometer.

## REFERENCES

1. Poole, C.F. and Schuette, S.A., *Contemporary Practice of Chromatography*, Elsevier Science Publishers, Amsterdam, 1984.
2. Snyder, L.R. and Kirkland, J.J., *Introduction to Modern Liquid Chromatography*, John Wiley & Sons, New York, 1979.
3. Krstulovic, A.M. and Brown, P.R., *Reversed-Phase High Performance Liquid Chromatography*, John Wiley & Sons, New York, 1982.
4. *Basic Principles in Reversed Phase Chromatography*, Amersham Biosciences Online Education Centre, 2002.

Some Useful Ion-Pairing Agents	
Ion Type/Examples	Applications/Notes
Perchloric acid	Used for a wide range of basic analytes; typically used at 0.1 M concentration in reverse phase solvent system, and at approximately the same concentration in a water buffer system on the stationary phase in normal mode
Trifluoroacetic acid (TFA)	One of the most common ion-pairing agents used in HPLC; used for solutes that form positive ions; it is volatile and is therefore often easily removed; it has low absorption within detection wavelengths
Heptafluorobutyric acid (HFBA)	Used with analytes that form positive ions
Pentafluoro propionic acid (PFPA)	Used with analytes that form positive ions
Bis-(2-ethylhexyl) phosphate	Used for cationic species of intermediate polarity, such as phenols; typically used in reverse phase, on bis-(2-ethylhexyl) phosphoric acid/chloroform stationary phase at a pH $\approx$ 3.8
<i>N,N</i> -dimethyl protriptyline	Used for carboxylic acids; typically used in normal phase, with a basic (pH $\approx$ 9) buffered stationary phase and an organic mobile phase
Quaternary amines: tetramethyl, tetrabutyl, palmityltrimethyl-ammonium salts, usually in chloride or phosphate forms	Used for strong and weak acids, sulfonated dyes, carboxylic acids, in normal phase applications; typical buffer pH values are between 6 and 8.5, with an organic mobile phase; in reverse phase, the mobile phase is typically aqueous plus a polar organic modifier at nearly neutral pH values
Tertiary amines: tri- <i>n</i> -octyl amine	Used for carboxylic acids and sulfonates; used in reverse phase mode with a water + buffer + approximately 0.05 M perchloric acid mobile phase
Sulfonates, alkyl, and aromatic: methane or heptanesulfonate, camphorsulfonic acid	Used for strong and weak bases, benzalkonium salts, and catecholamines
Alkyl sulfates: octyl, decyl, dodecyl, and lauryl sulfates	Used in similar applications as the sulfonates, but provide a different selectivity; typically used in reverse phase mode, often using a water + methanol + sulfuric acid mobile phase

## MATERIALS COMPATIBLE WITH AND RESISTANT TO 72% PERCHLORIC ACID

The perchloric acid mentioned in the previous table on ion-pairing agents must be handled with great care since it can be a very powerful oxidizing agent. Cold perchloric acid at a concentration of 70% (mass/mass) or less is not considered a very strong oxidizing agent. At concentrations of 73% or higher, or at lower concentrations but at higher temperatures, perchloric acid is a powerful oxidant. The following table provides some guidance in handling this material in the laboratory.<sup>1</sup>

### REFERENCES

1. Furr, A.K., Ed., *CRC Handbook of Laboratory Safety*, 5th ed., CRC Press, Boca Raton, FL, 2000.

Material	Comments
Elastomers	
Gum rubber	Each batch must be tested to determine compatibility Slight swelling only
Vitons	
Metals and Alloys	
Tantalum	Excellent
Titanium (chemically pure grade)	Excellent
Zirconium	Excellent
Columbium (Niobium)	Excellent
Hastelloy	Slight corrosion rate
Plastics	
Polyvinyl chloride	
Teflon	
Polyethylene	
Polypropylene	
Kel-F	
Vinylidene fluoride	
Saran	
Epoxies	
Others	
Glass	
Glass-lined steel	
Alumina	
Fluorolube	

## Incompatible

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### Plastics

Polyamide (nylon)  
Modacrylic ester, Dynel (35–85%)  
acrylonitrile  
Polyester (dacron)  
Bakelite  
Lucite  
Micarta

### Others

Cellulose-based lacquers, metals  
Copper  
Copper alloys (brass, bronze, etc.) for very  
shock-sensitive perchlorate salts  
Aluminum (dissolves at room temperature)  
High nickel alloys (dissolves), others  
Cotton  
Wood  
Glycerin–lead oxide (letharge)

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## MORE COMMON HPLC STATIONARY PHASES

The following table provides a summary of the general characteristics of the most popular stationary phases used in modern high-performance liquid chromatography.<sup>1-7</sup> The most commonly used phases are the bonded reverse phase materials, in which separation control is a function of the mobile (liquid) phase. The selection of a particular phase and solvent system is an empirical procedure involving survey analyses. The references provided below will assist the reader in this procedure.

## REFERENCES

1. Snyder, L.R. and Kirkland, J.J., *Introduction to Modern Liquid Chromatography*, 2nd ed., John Wiley & Sons, New York, 1979.
2. Poole, C.F. and Schuette, S.A., *Contemporary Practice of Chromatography*, Elsevier, Amsterdam, 1984.
3. Krstulovic, A.M. and Brown, P.R., *Reverse-Phase High Performance Liquid Chromatography*, John Wiley & Sons (Interscience), New York, 1982.
4. Berridge, J.C., *Techniques for the Automated Optimization of HPLC Separations*, John Wiley & Sons, Chichester, 1985.
5. Braithwaite, A. and Smith, F.J., *Chromatographic Methods*, 4th ed., Chapman & Hall, London, 1985.
6. Sander, L.C., Sharpless, K.E., and Pursch, M., C-30 stationary phases for the analysis of food by liquid chromatography, *J. Chromatogr. A*, 880, 189, 2000.
7. Snyder, L.R., Kirkland, J.J., and Glajch, J.L., *Practical HPLC Method Development*, John Wiley & Sons, New York, 1997.

### More Common HPLC Stationary Phases

Phase Type	Bond Type	Functionality	Separation Mode	Notes and Applications
<b>Solid Sorbents</b>				
Silica (pure)	SiO <sub>2</sub>	Si–OH	Adsorption	Usually used with nonpolar mobile phase, since it is the most polar sorbent; selectivity is based on differences in number and location of polar groups; results can be unpredictable due to changes in the surface due to adsorption; water or acetic acid is often added (in low concentrations) to the mobile phase to better control surface characteristics; usually the best choice for normal phase and preparative-scale separations
Alumina, acidic	Al <sub>2</sub> O <sub>3</sub> –A	—	Adsorption, normal phase	Similar in characteristics and application to silica; a classic Lewis acid, lacking two electrons in the Al center, having an approximate pH of 4.5; this phase can be treated to make it more retentive to electron-rich species
Alumina, neutral	Al <sub>2</sub> O <sub>3</sub>		Adsorption, normal phase	Prepared as a neutral surface, approximate pH of 7.5; used for separation of aromatics and moieties that contain electronegative groups such as oxygen
Alumina, base treated	Al <sub>2</sub> O <sub>3</sub> –B		Adsorption, normal phase	Base treatment makes the phase suitable for separation of hydrogen bonding or cationic species; approximate pH of 10
Zirconia (pure)	ZrO <sub>2</sub>	—	Normal phase	Can be used over the entire pH range, 1–14; can be heated to 200°C; has a stable particle size that will not shrink; surface is free of silanol groups
Florisil	MgO <sub>3</sub> Si	—	Polar adsorbent	Florisil is a magnesium-substituted silica with a highly polar surface; typically has a relatively large particle size (approximately 200 μm), and therefore high flow rates are possible even with viscous samples; used with many official methods, and in cases where the Lewis acidity of alumina would be problematic
<b>Bonded Phases Straight Chain</b>				
ODS	Si–O–Si–C	Octadecyl, <i>n</i> -C <sub>18</sub> (CH <sub>2</sub> ) <sub>17</sub> CH <sub>3</sub> , hydrocarbon chain	Bonded, reverse phase	Octadecylsilane; most common material used in HPLC; high resolution possible; pH must be maintained between 2 and 7
C2	Si–O–Si–C	–CH <sub>2</sub> CH <sub>3</sub>	Moderately polar bonded, reverse phase	A moderately polar phase that is used for aqueous samples, blood and urine samples; moderate polarity derives from the polar substrate, silica; has a polarity similar to a cyclohexyl bonded phase
OS	Si–O–Si–C	Octyl, <i>n</i> -C <sub>8</sub> hydrocarbon chain	Bonded, reverse phase	Octylsilane; lower resolution than the octadecyl bonded phase; useful when separations involve species of greatly different polarities
C30	Si–O–Si–C	Triacetyl, <i>n</i> -C <sub>30</sub> hydrocarbon chain	Bonded, reverse phase	Useful for the separation of carotenoid compounds
TMS	Si–O–Si–C	Methyl, CH <sub>3</sub>	Bonded, reverse phase	Tetramethylsilane; lowest resolution of reverse phase packings; useful for survey separations and for large molecules

More Common HPLC Stationary Phases (continued)

Phase Type	Bond Type	Functionality	Separation Mode	Notes and Applications
<b>Bonded Phases, Functionalized<sup>a</sup></b>				
Bonded diol	Si–O–Si–C	$\begin{array}{cc} \text{OH} & \text{OH} \\   &   \\ -\text{C} & -\text{C}- \\ &   \end{array}$	Polar bonded phase	A polar phase that has a hydrogen bonding capability similar to that of unbonded silica; useful in size-exclusion chromatography and in the analysis of glycols and glycerol, oils, lipids, and related compounds
Carboxylic acid (CBA)	Si–O–Si–C	–CH <sub>2</sub> CH <sub>2</sub> COOH	Polar bonded phase	Medium-polarity phase that has a weak cation exchange capability useful for strong cations; above pH of 4.8, most of the functional groups are negatively charged, and therefore the phase can be used for cationic compounds; lowering pH to 2.8 elutes retained analytes
Cyclohexyl (CH)	Si–O–Si–C	–C <sub>6</sub> H <sub>11</sub>	Moderately polar bonded phase	A moderately polar phase that is used for aqueous samples; moderate polarity derives from the polar substrate, silica; has a polarity similar to a C2 bonded phase
Bonded nitrile	Si–O–Si–C	–CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> –C≡N	Moderately polar bonded phase	Moderate polar phase, but with selectivity modified with respect to silica; less sensitive to mobile phase impurities than silica; also called cyanopropyl phase
Bonded nitro	Si–O–Si–C	–NO <sub>2</sub>	Polar bonded phase	Selectivity is modified with respect to silica through the aminopropyl functionality; the propyl linkage can interact with nonpolar interactions; highly polar phase overall; phase is less stable than cyano or diol phases; can utilize hydrogen bonding and ion exchange mechanisms; protonates below pH of 9.8; useful for sugar and carbohydrate separations; not recommended for samples that contain aldehydes and ketones
Bonded amine	Si–O–Si–C	–CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> –NH <sub>2</sub>	Polar bonded phase	
Phenyl	Si–O–Si–C	–φ	Normal or reverse phase	Lower efficiency than other bonded phases; more polar than ODS, OS, and TMS phases; used with both normal and reverse phase solvent systems
Polybutadiene	Zr–C	$\begin{array}{c} \text{[CH}_2\text{C(CH}_2\text{)}\text{CH=CH}_2\text{]}_n \\ \text{H} \qquad \qquad \text{H} \end{array}$	Reverse phase	Similar to ODS in separation characteristics; can be used up to 150°C
Carbon on zirconia	Zr–C		Reverse phase	Elemental carbon on zirconia that is useful in the separation of diastereomers
Polystyrene on zirconia	Zr–C		Reverse phase	Separations are similar to those obtained with phenyl bonded silica; can be used up to 150°C

<sup>a</sup> In this context, *functionalized* refers to functionalization beyond straight-chain hydrocarbons.

φ denotes a phenyl group.



**More Common HPLC Stationary Phases (continued)**

Phase Type	Bond Type	Functionality	Separation Mode	Notes and Applications
<b>Bonded Phases, Ion Exchange</b>				
Bonded amine	Si–O–Si–C	$\text{CH}_2\text{CH}_2\text{CH}_2\text{--NH}_2$	Polar bonded phase	Selectivity is modified with respect to silica through the aminopropyl functionality; the propyl linkage can interact via nonpolar interactions; highly polar phase overall; phase is less stable than cyano or diol phases; can utilize hydrogen bonding and ion exchange mechanisms, and as such is a weak anion exchanger; protonates below pH = 9.8; useful for sugar and carbohydrate separations; not recommended for samples that contain aldehydes and ketones
Benzene sulfonic acid	Si–O–Si–C	$\text{CH}_2\text{CH}_2\phi\text{--SO}_3^-\text{H}^+$	Ion exchange	Separates cations, with divalent ions more strongly retained than monovalent ions; phosphate buffer systems are often used, sometimes with low concentrations of polar nonaqueous modifiers added; the presence of the benzene group on the benzenesulfonic acid moiety gives this phase a dual nature, and the ability to separate based upon nonpolar interactions
Propyl, ethylene diamine	Si–O–Si–C	$\text{--CH}_2\text{CH}_2\text{CH}_2\text{--NHCH}_2\text{CH}_2\text{NH}_2$	Ion exchange	Weak anion exchange phase for aqueous and biological samples; incorporates a bidentate ligand to form chelate complexes useful for metal separations; less polar than the propyl amine bonded phase
Propyl sulfonic acid	Si–O–Si–C	$\text{--CH}_2\text{CH}_2\text{CH}_2\text{--SO}_3^-\text{Na}^+$	Ion exchange	Strong cation exchange substrate for aqueous and biological samples; effective for the separation of weaker cations such as pyridinium compounds
Propyl, trimethylamino	Si–O–Si–C	$\text{--CH}_2\text{CH}_2\text{CH}_2\text{--N}^+(\text{CH}_3)_2\text{Cl}^-$	Ion exchange	Strong anion exchange phase for aqueous and biological samples suitable for weaker anions such as carboxylic acids; properties may be modified or conditioned by proper formulation of buffer mobile phases (see the appropriate table in the Solution Properties chapter)

*Note:* While the principal separation mechanism is ion exchange, the organic moieties on many of these phases can interact through nonpolar interactions as well. Thus, many phases are mixed mode.

$\phi$  denotes a phenyl group.

## ELUOTROPIC VALUES OF SOLVENTS ON OCTADECYLSILANE

The following table provides, for comparative purposes, eluotropic values on bonded octadecyl silane (ODS) and octyl silane (OS) for common solvents.<sup>1,2</sup>

### REFERENCES

1. Krieger, P.A., *High Purity Solvent Guide*, Burdick and Jackson Laboratories, McGaw Park, IL, 1984.
2. Ahuja, S., *Trace and Ultratrace Analysis by HPLC*, John Wiley & Sons, New York, 1992.

**Eluotropic Values of Solvents on Octadecylsilane**

Solvent	Eluotropic Value, ODS	Eluotropic Value, OS
Acetic acid	—	2.7
Acetone	8.8	9.3
Acetonitrile	3.1	3.3
1,4-Dioxane	11.7	13.5
Dimethyl formamide	7.6	9.4
Methanol	1.0	1.0
Ethanol	3.1	3.2
1-Propanol	10.1	10.8
2-Propanol	8.3	8.4
Tetrahydrofuran	3.7	—

## MESH-SIZE RELATIONSHIPS

The following table provides the relationship between particle sizes and standard sieve mesh sizes. It should be noted, however, that the trend in HPLC has been toward shorter columns containing much finer particles than the standard sieves will separate. These values will be of use when packing relatively large-diameter columns for bench-top elutions, however. See page 13 for additional information.

Mesh-Size Relationships				
Mesh Range	Top Screen Opening, $\mu\text{m}$	Bottom Screen Opening, $\mu\text{m}$	Micron Screen, $\mu\text{m}$	Range Ratio
80/100	177	149	28	1.19
100/120	149	125	24	1.19
100/140	149	105	44	1.42
120/140	125	105	20	1.19
140/170	105	88	17	1.19
170/200	88	74	14	1.19
200/230	74	63	11	1.19
230/270	63	53	10	1.19
270/325	53	44	9	1.20
325/400	44	37	7	1.19

## EFFICIENCY OF HPLC COLUMNS

The efficiency of a column used for HPLC describes the ability of the column to produce sharp, narrow peaks. Typically, the efficiency is represented at the plate number,  $N$ . The plate number can be estimated by

$$N = 3500 L/d_p$$

where  $L$  is the column length in cm and  $d_p$  is the particle diameter in  $\mu\text{m}$ . The following table provides the plate number for optimized test conditions for various combinations of column length and particle diameter. It therefore represents the upper limit of efficiency and can be used as a column diagnostic measurement.<sup>1</sup>

## REFERENCES

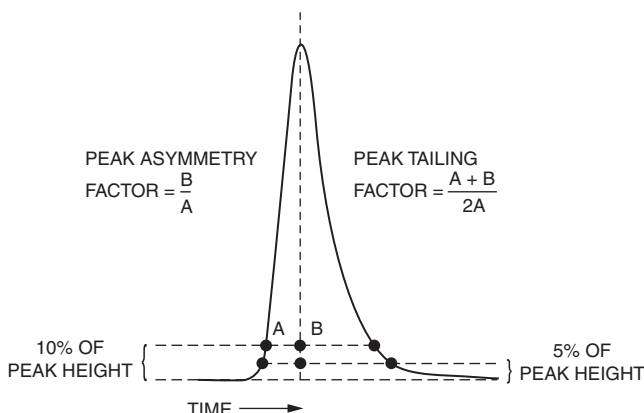
1. Snyder, L.R., Kirkland, J.J., and Glajch, J.L., *Practical HPLC Method Development*, 2nd ed., John Wiley & Sons, New York, 1997.

Efficiency of HPLC Columns		
Particle Diameter, $\mu\text{m}$	Column Length, cm	Plate Number
10	15	6000–7000
10	25	8000–10,000
5	10	7000–9000
5	15	10,000–12,000
5	25	17,000–20,000
3	5	6000–7000
3	7.5	9000–11,000
3	10	12,000–14,000
3	15	17,000–20,000

From Snyder, L.R., Kirkland, J.J., and Glajch, J.L., *Practical HPLC Method Development*, 2nd ed., John Wiley & Sons, New York, 1997. With permission.

## COLUMN FAILURE PARAMETERS

The point at which a column used for HPLC will fail depends largely upon how the operator uses it. Eventually, however, all HPLC columns will fail. The onset of column failure can be monitored by two common failure parameters: the peak asymmetry factor,  $A_s$ , and the peak tailing factor. These parameters are defined according to the figure below:



The two parameters are related, and the following tables provide the interconversion.<sup>1</sup>

## REFERENCES

1. Snyder, L.R., Kirkland, J.J., and Glajch, J.L., *Practical HPLC Method Development*, 2nd ed., John Wiley & Sons, New York, 1997.

Peak Asymmetry Factor ( $A_s$ , 10%)	Peak Tailing Factor (5%)
1.0	1.0
1.3	1.2
1.6	1.4
1.9	1.6
2.2	1.8
2.5	2.0

From Snyder, L.R., Kirkland, J.J., and Glajch, J.L., *Practical HPLC Method Development*, 2nd ed., John Wiley & Sons, New York, 1997. With permission.

To put these factors into context, column performance can be described as in the following table:

Peak Asymmetry Factor ( $A_s$ , 10%)	Column Performance
1.0–1.05	Excellent, new
1.2	Acceptable
2.0	Degraded, approaching poor
4.0	Not usable

From Snyder, L.R., Kirkland, J.J., and Glajch, J.L., *Practical HPLC Method Development*, 2nd ed., John Wiley & Sons, New York, 1997. With permission.

## SPECIALIZED STATIONARY PHASES FOR LIQUID CHROMATOGRAPHY

The following table provides information on the properties and applications of some of the more specialized bonded, adsorbed, and polymeric phases used in modern high-performance liquid chromatography. In many cases, the phases are not commercially available; refer to the appropriate literature citation for details on the synthesis.

### REFERENCES

1. Pietrzyk, D.J. and Cahill, W.J., Amberlite XAD-4 as a stationary phase for preparative liquid chromatography in a radially compressed column, *J. Liq. Chromatogr.*, 5, 781, 1982.
2. Nikolov, Z., Meagher, M., and Reilly, P., High-performance liquid chromatography of trisaccharides on amine-bonded silica columns, *J. Chromatogr.*, 321, 393, 1985.
3. Ascalone, V. and Dal Bo, L., Determination of ceftriaxone, a novel cephalosporin, in plasma, urine and saliva by high-performance liquid chromatography on an  $\text{NH}_2$  bonded-phase column, *J. Chromatogr.*, 273, 357, 1983.
4. Pharr, D.Y., Uden, P.C., and Siggia, S., A 3-(p-acetylphenoxy) propylsilane bonded phase for liquid chromatography of basic amines and other nitrogen compounds, *J. Chromatogr. Sci.*, 23, 391, 1985.
5. Felix, G. and Bertrand, C., Separation of polyaromatic hydrocarbons on caffeine-bonded silica gel, *J. Chromatogr.*, 319, 432, 1985.
6. Felix, G., Bertrand, C., and Van Gastel, F., A new caffeine bonded phase for separation of polyaromatic hydrocarbons and petroleum asphaltenes by high-performance liquid chromatography, *Chromatographia*, 20, 155, 1985.
7. Bruner, F., Berton, G., and Ciccioli, P., Comparison of physical and gas chromatographic properties of Sterling FT and Carbo-pack-C graphitized carbon blacks, *J. Chromatogr.*, 120, 307, 1976.
8. Bruner, F., Ciccioli, P., Crescentini, G., and Pistolesi, M.T., Role of the liquid phase in gas-liquid-solid chromatography and its influence on column performance: an experimental approach, *Anal. Chem.*, 45, 1851, 1973.
9. Ciccioli, P. and Liberti, A., Microbore columns packed with graphitized carbon black for high-performance liquid chromatography, *J. Chromatogr.*, 290, 173, 1984.
10. DiCorcia, A., Liberti, A., and Samperi, R., Gas-liquid-solid chromatography-theoretical aspects and analysis of polar compounds, *Anal. Chem.*, 45, 1228, 1973.
11. Hatada, K., Kitayama, T., Shimizu, S.-I., Yuki, H., Harris, W., and Vogl, O., High-performance liquid chromatography of aromatic compounds on polychloral, *J. Chromatogr.*, 248, 63, 1982.
12. Abe, A., Tasaki, K., Inomata, K., and Vogl, O., Confirmational rigidity of polychloral: effect of bulky substituents on the polymerization mechanism, *Macromolecules*, 19, 2707, 1986.
13. Kubisa, P., Corley, L.S., Kondo, T., Jacovic, M., and Vogl, O., Haloaldehyde polymers. XXIII. Thermal and mechanical properties of chloral polymers, *Pol. Eng. Sci.*, 21, 829, 1981.
14. Veuthey, J.-L., Bagnoud, M.-A., and Haerdi, W., Enrichment of amino and carboxylic acids using copper-loaded silica pre-columns coupled on-line with HPLC, *Intern. J. Environ. Anal. Chem.*, 26, 157, 1986.
15. Guyon, F., Foucault, A., Caude, M., and Rosset, R., Separation of sugars by h.p.l.c. on copper silicate gel, *Carbohydr. Res.*, 140, 135, 1985.
16. Leonard, J.L., Guyon, F., and Fabiani, P., High-performance liquid chromatography of sugars on copper (II) modified silica gel, *Chromatographia*, 18, 600, 1984.
17. Yamazaki, S., Omori, H., and Eon Oh, C., High performance liquid chromatography of alkaline-earth metal ions using reversed-phase column coated with N-n-dodecyliminodiacetic acid, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 9, 765, 1986.
18. Miller, N.T. and Shieh, C.H., Preparative hydrophobic interaction chromatography of proteins using ether based chemically bonded phases, *J. Liq. Chromatogr.*, 9, 3269, 1986.
19. Williams, R.C., Vasta-Russell, J.F., Glajch, J.L., and Golebiowski, K., Separation of proteins on a polymeric fluorocarbon high-performance liquid chromatography column packing, *J. Chromatogr.*, 371, 63, 1986.

20. Hirayama, C., Ihara, H., Yoshinga, T., Hirayama, H., and Motozato, Y., Novel packing for high pressure liquid chromatography: partially alkylated and cross-linked PMLG spherical particles, *J. Liq. Chromatogr.*, 9, 945, 1986.
21. Kawasaki, T., Kobayashi, W., Ikeda, K., Takahashi, S., and Monma, H., High-performance liquid chromatography using spherical aggregates of hydroxyapatite micro-crystals as adsorbent, *Eur. J. Biochem.*, 157, 291, 1986.
22. Kawasaki, T. and Kobayashi, W., High-performance liquid chromatography using novel square tile-shaped hydroxyapatite crystals as adsorbent, *Biochem. Int.*, 14, 55, 1987.
23. Funae, Y., Wada, S., Imaoka, S., Hirotsune, S., Tominaga, M., Tanaka, S., Kishimoto, T., and Maekawa, M., Chromatographic separation of  $\alpha$ -acid glyco-protein from  $\alpha$ -antitrypsin by high-performance liquid chromatography using a hydroxyapatite column, *J. Chromatogr.*, 381, 149, 1986.
24. Kadoya, T., Isobe, T., Ebihara, M., Ogawa, T., Sumita, M., Kuwahara, H., Kobayashi, A., Ishikawa, T., and Okuyama, T., A new spherical hydroxyapatite for high performance liquid chromatography of proteins, *J. Liq. Chromatogr.*, 9, 3543, 1986.
25. Kawasaki, T., Niikura, M., Takahashi, S., and Kobayashi, W., High-performance liquid chromatography using improved spherical hydroxyapatite particles as adsorbent: efficiency and durability of the column, *Biochem. Int.*, 13, 969, 1986.
26. Bernardi, G., Chromatography of nucleic acids on hydroxyapatite columns, *Methods Enzymol.*, 21D, 95, 1971.
27. Bernardi, G., Chromatography of proteins on hydroxyapatite, *Methods Enzymol.*, 27, 471, 1973.
28. Bernardi, G., Chromatography of proteins on hydroxyapatite, Conference proceedings, *Methods Enzymol.*, 22, 325, 1971.
29. Figueroa, A., Corradini, C., Feibush, B., and Karger, B., High-performance immobilized-metal affinity chromatography of proteins on iminodiacetic acid silica-based bonded phases, *J. Chromatogr.*, 371, 335, 1986.
30. Danielson, N.D., Ahmed, S., Huth, J.A., and Targrove, M.A., Characterization of organomagnesium modified Kel-f polymers as column packings, *J. Liq. Chromatogr.*, 9, 727, 1986.
31. Taylor, P.J. and Sherman, P.L., Liquid crystals as stationary phases for high performance liquid chromatography, *J. Liq. Chromatogr.*, 3, 21, 1980.
32. Taylor, P.J. and Sherman, P.L., Liquid crystals as stationary phases for high performance liquid chromatography, *J. Liq. Chromatogr.*, 2, 1271, 1979.
33. Felix, G. and Bertrand, C., HPLC on pentafluorobenzamidopropyl silica gel, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 8, 362, 1985.
34. Kurosu, Y., Kawasaki, H., Chen, X.-C., Amano, Y., Fang, Y.-I., Isobe, T., and Okuyama, T., Comparison of retention times of polypeptides in reversed phase high performance liquid chromatography on polystyrene resin and on alkyl bonded silica, *Bunseki Kagaku*, 33, E301, 1984.
35. Yang, Y.-B. and Verzele, M., New water-compatible modified polystyrene as a stationary phase for high-performance liquid chromatography, *J. Chromatogr.*, 387, 197, 1987.
36. Nieminen, N. and Heikkilä, P., Simultaneous determination of phenol, cresols and xylenols in workplace air, using a polystyrene-divinylbenzene column and electrochemical detection, *J. Chromatogr.*, 360, 271, 1986.
37. Yang, Y.B., Nevejans, F., and Verzele, M., Reversed-phase and cation-exchange chromatography on a new poly(styrenedivinylbenzene) high capacity, weak cation-exchanger, *Chromatographia*, 20, 735, 1985.
38. Tweeten, K.A. and Tweeten, T.N., Reversed-phase chromatography of proteins on resin-based wide-pore packings, *J. Chromatogr.*, 359, 111, 1986.
39. Lee, D.P. and Lord, A.D., A high performance phase for the organic acids, *LC-GC*, 5, 261, 1987.
40. Miyake, K., Kitaura, F., Mizuno, N., and Terada, H., Determination of partition coefficient and acid dissociation constant by high-performance liquid chromatography on porous polymer gel as a stationary phase, *Chem. Pharm. Bull.*, 35, 377, 1987.
41. Joseph, J.M., Selectivity of poly(styrene-divinylbenzene) columns, *ACS Symp. Ser.*, 297, 83, 1986.
42. Cope, M.J. and Davidson, I.E., Use of macroporous polymeric high-performance liquid chromatographic columns in pharmaceutical analysis, *Analyst*, 112, 417, 1987.

43. Werkhoven-Goewie, C.E., Boon, W.M., Praat, A.J.J., Frei, R.W., Brinkman, U.A. Th., and Little, C.J., Preconcentration and LC analysis of chlorophenols, using a styrene-divinyl-benzene copolymeric sorbent and photochemical reaction detection, *Chromatographia*, 16, 53, 1982.
44. Smith, R.M., Selectivity comparisons of polystyrenedivinylbenzene columns, *J. Chromatogr.*, 291, 372, 1984.
45. Köhler, J., Poly(vinylpyrrolidone)-coated silica: a versatile, polar stationary phase for h.p.l.c., *Chromatographia*, 21, 573, 1986.
46. Murphy, L.J., Siggia, S., and Uden, P.C., High-performance liquid chromatography of nitroaromatic compounds on an N-propylaniline bonded stationary phase, *J. Chromatogr.*, 366, 161, 1986.
47. Felix, G. and Bertrand, C., HPLC on n-propyl picryl ether silica gel, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 7, 714, 1984.
48. Risner, C.H. and Jezorek, J.R., The chromatographic interaction and separation of metal ions with 8-quinolinol stationary phases in several aqueous eluents, *Anal. Chem. Acta*, 186, 233, 1986.
49. Shahwan, G.J. and Jezorek, J.R., Liquid chromatography of phenols on an 8-quinolinol silica gel-iron (III) stationary phase, *J. Chromatogr.*, 256, 39, 1983.
50. Krauss, G.-J., Ligand-exchange h.p.l.c. of uracil derivatives on 8-hydroxyquinoline-silica-polyol, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 9, 419, 1986.
51. Hansen, S.A., Helboe, P., and Thomsen, M., High-performance liquid chromatography on dynamically modified silica, *J. Chromatogr.*, 360, 53, 1986.
52. Helboe, P., Separation of corticosteroids by high-performance liquid chromatography on dynamically modified silica, *J. Chromatogr.*, 366, 191, 1986.
53. Hansen, D.H., Helboe, P., and Thomsen, M., Dynamically modified silica: the use of bare silica in reverse-phase high-performance liquid chromatography, *Trends Anal. Chem.*, 4, 233, 1985.
54. Flanagan, R.J., High-performance liquid chromatographic analysis of basic drugs on silica columns using non-aqueous ionic eluents, *J. Chromatogr.*, 323, 173, 1985.
55. Vespalec, R., Ciganková, M., and Viska, J., Effect of hydrothermal treatment in the presence of salts on the chromatographic properties of silica gel, *J. Chromatogr.*, 354, 129, 1986.
56. Unger, K.K., Jilge, G., Kinkel, J.N., and Hearn, M.T.W., Evaluation of advanced silica packings for the separation on biopolymers by high-performance liquid chromatography, *J. Chromatogr.*, 359, 61, 1986.
57. Lullmann, C., Genieser, H.-G., and Jastorff, B., Structural investigations on reversed-phase silicas, *J. Chromatogr.*, 354, 434, 1986.
58. Schou, O. and Larsen, P., Preparation of 6,9,12-trioxatridecylmethylsilyl substituted silica, a new stationary phase for liquid chromatography, *Acta Chem. Scand.*, B35, 337, 1981.
59. Desideri, P.G., Lepri, L., Merlini, L., and Checchini, L., High-performance liquid chromatography of amino acids and peptides on silica coated with ammonium tungstophosphate, *J. Chromatogr.*, 370, 75, 1986.



## Specialized Stationary Phases for Liquid Chromatography

**Name:** Amberlite XAD-4

**Structure:** Macroporous polystyrene-divinylbenzene nonpolar adsorbent, 62–177  $\mu\text{m}$  particle size

**Analytical Properties:** Used mainly in preparative-scale HPLC; stable over entire pH range (1–13); sometimes difficult to achieve column-to-column reproducibility due to packing the irregular particles; relatively lower efficiency than alkyl bonded phases; particles tend to swell as the organic content of the mobile phase increases

**Reference:** 1

**Name:** Amine bonded phase

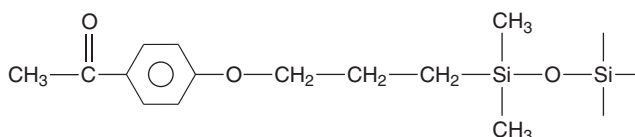
**Structure:**  $\text{NH}_2$  functionality with an Si–O–Si–C or Si–C linkage

**Analytical Properties:** Polar phase useful for sugar and carbohydrate separation; not recommended for samples that contain aldehydes and ketones

**Reference:** 2, 3

**Name:** 3-(*p*-Acetylphenoxy) propyl bonded phase

**Structure:**

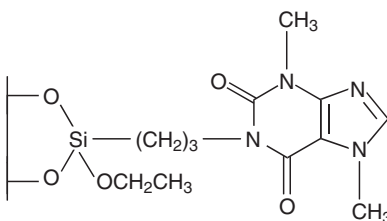


**Analytical Properties:** Selective for aromatic amines, with the selectivity being determined by the interactions with the carbonyl group

**Reference:** 4

**Name:** Caffeine bonded phase

**Structure:**



**Analytical Properties:** Separation of polynuclear aromatic hydrocarbons (of the type often encountered in petroleum residue work) by donor–acceptor complex formation

**Reference:** 5, 6

**Name:** Graphitized carbon black

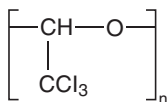
**Structure:** Carbon subjected to +1300°C in helium atmosphere, resulting in a graphite-like structure in the form of polyhedra, with virtually no unsaturated bonds, ions, lone electron pairs, or free radicals

**Analytical Properties:** Especially for use in microbore columns; suggested for lower aromatics but with some potential for higher-molecular-mass compound separations

**Reference:** 7–10

**Name:** Polychloral (polytrichloroacetaldehyde)

**Structure:**



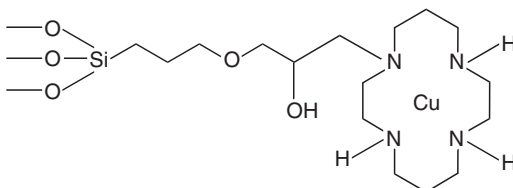
## Specialized Stationary Phases for Liquid Chromatography (continued)

**Analytical Properties:** Separation of lower aromatic hydrocarbons and small fused-ring systems using toluene and hexane methanol as the stationary phases; the relatively low pressure rating on the polymeric phase limits solvent flow rate

**Reference:** 11–13

**Name:** Cyclam-copper-silica

**Structure:**

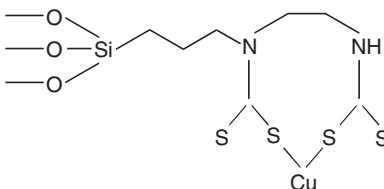


**Analytical Properties:** This phase has found use in preconcentrating carboxylic acids on precolumns

**Reference:** 14

**Name:** Bis-dithiocarbamate-copper-silica

**Structure:**



**Analytical Properties:** This phase has found use in preconcentrating amino acids on precolumns

**Reference:** 14

**Name:** Copper (II) coated silica gel

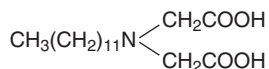
**Structure:**  $(\text{--Si--O})_2\text{Cu}(\text{NH}_3)_x(\text{H}_2\text{O})_y$   
x = 1 or 2

**Analytical Properties:** Separation of sugars and amino sugars by ligand exchange or partitioning interactions using water + acetonitrile + ammonia liquid phases; the phase is usually prepared by treating silica gel with ammoniacal copper sulfate solution prior to packing

**Reference:** 15, 16

**Name:** *N*-*n*-Dodecyliminodiacetic acid

**Structure:**



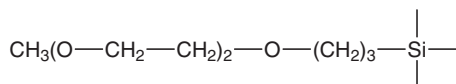
(coated on silica gel)

**Analytical Properties:** Separation of alkaline-earth metal ions

**Reference:** 17

**Name:** Ether bonded phase

**Structure:**



on 15- to 20- $\mu\text{m}$ -wide pore silica

**Analytical Properties:** Separation by hydrophobic interaction chromatography, using aqueous salt solutions near pH = 7; used primarily in protein work

**Reference:** 18

### Specialized Stationary Phases for Liquid Chromatography (continued)

**Name:** Fluorocarbon polymer phase

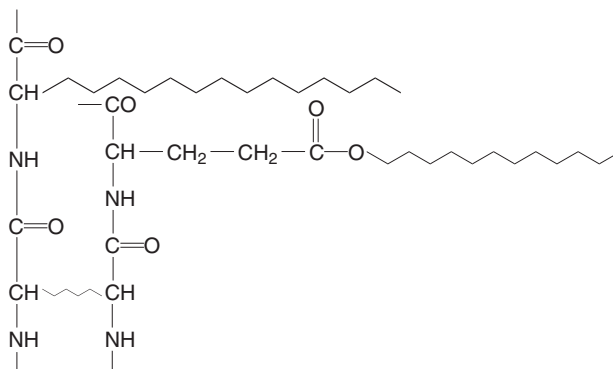
**Structure:** Proprietary information of E.I. duPont de Nemours Corp.

**Analytical Properties:** Similar separations as obtained using  $C_3$  bonded silica, with a much larger pH stability range than silica-based phases; useful for protein and peptide separations using TFA (trifluoroacetic acid) as a mobile phase modifier; less mechanical stability than silica-based phases

**Reference:** 19

**Name:** Poly( $\gamma$ -methyl-L-glutamate) (PMLG)

**Structure:** Partially cross-linked, with long-chain alkyl branches:



**Analytical Properties:** Separation similar to ODS, but with somewhat higher stability in alkaline solutions; particles are spherical and macroporous

**Reference:** 20

**Name:** Hydroxyapatite adsorbent

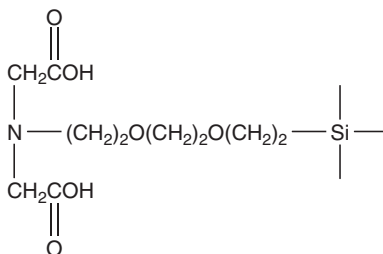
**Structure:**  $Ca_{10}(PO_4)_6(OH)_2$  crystalline, nonstoichiometric mineral rich in surface ions (primarily carbonate)

**Analytical Properties:** Separation of proteins; overcomes some difficulties associated with ion exchange; selectivity and efficiency depend to some extent on particle geometry (i.e., sphere, plate, etc.)

**Reference:** 21–29

**Name:** Iminodiacetic acid bonded phase

**Structure:**



**Analytical Properties:** Separation of proteins by immobilized-metal affinity chromatography (HPIMAC) with  $Cu(II)$  or  $Zn(II)$  present in the mobile phase

**Reference:** 29

**Name:** Kel-F (polychlorotrifluoroethylene)

**Structure:** Exact structure is proprietary, 3M Company

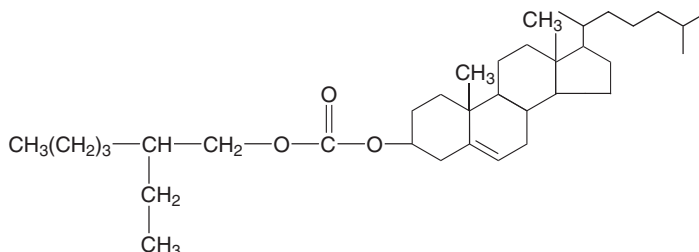
**Analytical Properties:** Highly inert, even more nonpolar than hydrocarbon phases, with sufficient mechanical integrity to withstand high pressures; can be functionalized with  $-CH_3$ ,  $CH_3(CH_2)_3-$ , and phenyl (using Grignard reactions) to increase selectivity

**Reference:** 30

### Specialized Stationary Phases for Liquid Chromatography (continued)

**Name:** 2-Ethylhexyl carbonate coated or bonded on cholesteryl silica (room temperature liquid crystal)

**Structure:**

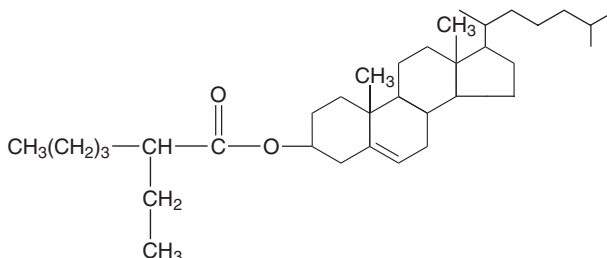


**Analytical Properties:** Has been used for the separation of estrogens and corticoid steroids; liquid crystal phase retains some order when coated on an active substrate

**Reference:** 31, 32

**Name:** Cholesteryl-2-ethylhexanoate (room temperature liquid crystal) on silica

**Structure:**

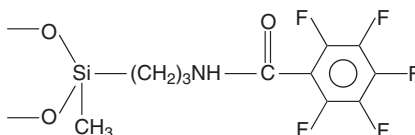


**Analytical Properties:** Has been used for the separation of androstenediones and testosterone

**Reference:** 31, 32

**Name:** Pentafluorobenzamidopropyl silica gel

**Structure:**

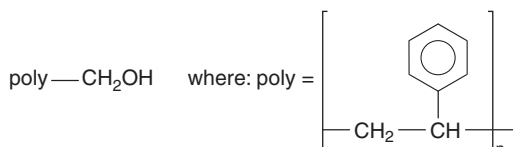


**Analytical Properties:** Separations via interactions with  $\pi$ -electrons of solutes; can be used in both normal and reverse phase for such  $\pi$ -donor systems as polynuclear aromatic hydrocarbons

**Reference:** 33

**Name:** Hydroxymethyl polystyrene

**Structure:**



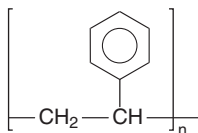
**Analytical Properties:** Separation of polypeptides; usually gives shorter retention times than ODS; hydrophobic interactions not as strong as with ODS

**Reference:** 34

## Specialized Stationary Phases for Liquid Chromatography (continued)

**Name:** Polystyrene

**Structure:**

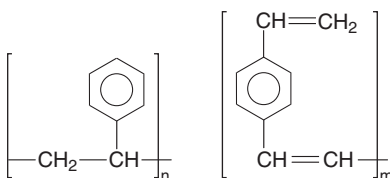


**Analytical Properties:** Separation of polypeptides with results similar to those obtainable with ODS; higher stability at high pH levels (to allow the phase to be washed); stronger hydrophobic interactions than ODS in reverse phase mode

**Reference:** 35

**Name:** Polystyrene-divinylbenzene (PS-DVB)

**Structure:** Exact structure is proprietary

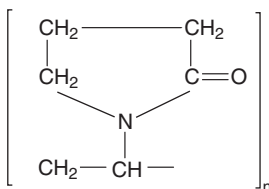


**Analytical Properties:** Useful for the separation of relatively polar compounds such as phenols, carboxylic acids, organic anions, nucleosides, alkylarylketones, chlorophenols, barbiturates, thiamine derivatives; good stability under high and low pH; reasonable mechanical integrity at high carrier pressure; compatible with buffered liquid phases

**Reference:** 36–44

**Name:** Poly(*N*-vinylpyrrolidone) (PVP) on silica

**Structure:**

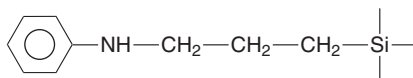


**Analytical Properties:** Separates aromatic and polynuclear aromatic hydrocarbons; can be used in normal phase mode (commonly using *n*-heptane or *n*-heptane + dichloromethane liquid phases) or reverse phase mode (commonly using methanol + water, acetonitrile + water, or phosphate-buffered liquid phases)

**Reference:** 45

**Name:** Bonded *n*-propylaniline

**Structure:**



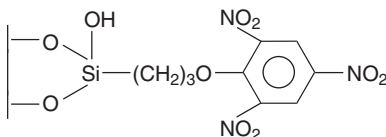
**Analytical Properties:** Selectivity is based on charge transfer interactions; nitroaromatic compounds are separated essentially according to the number of nitro groups, the higher number compounds being most strongly retained when using methanol/water mobile phases

**Reference:** 46

### Specialized Stationary Phases for Liquid Chromatography (continued)

**Name:** *n*-Propylpicrylether bonded phase

**Structure:**

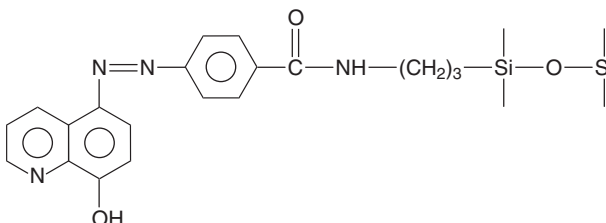


**Analytical Properties:** Separation of aromatic species, including polynuclear aromatic species, by charge transfer interactions

**Reference:** 47

**Name:** 8-Quinolinol bonded phases

**Structure:**

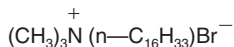


**Analytical Properties:** Separates phenols and EPA priority pollutants; often used with metal ions (such as iron (III)) as chelate ligands; 8-quinolinol has a high affinity for oxygen moieties and will form complexes with upwards of 60 metal ions; often with an acidic aqueous mobile phase

**Reference:** 48–50

**Name:** Cetyltrimethyl ammonium bromide adsorbed on silica

**Structure:**

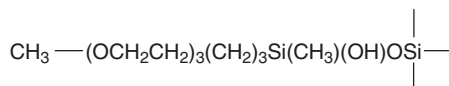


**Analytical Properties:** Has been used to separate aromatic hydrocarbons, heterocyclic compounds, phenols, and aryl amines using methanol/water/phosphate buffer; extent of adsorption affects retention times; also used as a mobile phase modifier to provide a dynamically modified silica

**Reference:** 51–57

**Name:** 6,9,12-Trioxatridecylmethyl bonded phase

**Structure:**



**Analytical Properties:** Phase is very well wetted by water, allowing mobile phases with high water concentration to be used; somewhat higher efficiency and selectivity than ODS, but with similar separation properties

**Reference:** 58

**Name:** Ammonium tungstophosphate on silica

**Structure:** Tungstophosphoric acid with ammonium nitrate

**Analytical Properties:** Separation of compounds containing the  $NH_4^+$  group, such as amino acids and peptides; the coated silica also behaves as a reverse phase for the separation of aliphatic and aromatic acids; high selectivity for glycine and tyrosine oligomers

**Reference:** 59

## CHIRAL STATIONARY PHASES FOR LIQUID CHROMATOGRAPHY

The following table provides information on the properties and applications of some of the more specialized stationary phases used to carry out the separation of enantiomeric mixtures. In many cases, the phases are not commercially available. Refer to the appropriate literature citation for details on the synthesis.

### REFERENCES

#### General References

1. Armstrong, D.W., Chiral stationary phases for high performance liquid chromatographic separation of enantiomers: a mini-review, *J. Liq. Chromatogr.*, 7, 353, 1984.
2. Dappen, R., Arm, H., and Meyer, V.R., Applications and limitations of commercially available chiral stationary phases for high-performance liquid chromatography, *Chromatogr. Rev.*, 200, 1, 1986.
3. Armstrong, D.W., Chen, S., Chang, C., and Chang, S., A new approach for the direct resolution of racemic beta adrenergic blocking agents by HPLC, *J. Liq. Chromatogr.*, 15, 545, 1992.
4. Armstrong, D.W., The evolution of chiral stationary phases for liquid chromatography, *J. Chin. Chem. Soc.*, 45, 581, 1998.
5. *Cyclobond Handbook: A Guide to Understanding Cyclodextrin Bonded Phases for Chiral LC Separations*, 6th ed., Advanced Separation Technologies, Wippany, NJ, 2002.
6. *Chirobiotic Handbook: A Guide to Using Macrocyclic Glycopeptide Bonded Phases for Chiral LC Separations*, 4th ed., Advanced Separation Technologies, Wippany, NJ, 2002.

#### Cited References

1. Erlandsson, P., Hansson, L., and Isaksson, R., Direct analytical and preparative resolution of enantiomers using albumin adsorbed to silica as a stationary phase, *J. Chromatogr.*, 370, 475, 1986.
2. Kuesters, E. and Giron, D., Enantiomeric separation of the beta-blocking drugs pindolol and bipindolol using a chiral immobilized protein stationary phase, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 9, 531, 1986.
3. Hermansson, J. and Eriksson, M., Direct liquid chromatographic resolution of acidic drugs using a chiral 1-acid glycoprotein column (Enantiopac), *J. Liq. Chromatogr.*, 9, 621, 1986.
4. Naobumi, O. and Hajimu, K., HPLC separation of amino acid enantiomers on urea derivatives of L-valine bonded to silica gel, *J. Chromatogr.*, 285, 198, 1984.
5. Okamoto, Y., Sakamoto, H., Hatada, K., and Irie, M., Resolution of enantiomers by HPLC on cellulose trans- and cis-tris (4-phenylazophenylcarbamate), *Chem. Lett.*, 6, 983, June 1986.
6. Ichid, A., Shibata, T., Okamoto, I., Yuki, Y., Namikoshi, H., and Toga, Y., Resolution of enantiomers by HPLC on cellulose derivatives, *Chromatographia*, 19, 280, 1984.
7. Tagahara, K., Koyama, J., Okatani, T., and Suzuta, Y., Chromatographic resolution of racemic tetrahydroberberine alkaloids by using cellulose tris (phenylcarbamate) stationary phase, *Chem. Pharm. Bull.*, 34, 5166, 1986.
8. Klemisch, W. and von Hodenberg, A., Separation on crosslinked acetylcellulose, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 9, 765, 1986.
9. Rimbock, K., Kastner, F., and Mannschreck, A., Microcrystallinetribenzoyl cellulose: a high-performance liquid chromatographic sorbent for the separation of enantiomers, *J. Chromatogr.*, 351, 346, 1986.
10. Lindner, K. and Mannschreck, A., Separation of enantiomers by high-performance liquid chromatography on triacetylcellulose, *J. Chromatogr.*, 193, 308, 1980.
11. Gubitz, G., Jellenz, W., and Schonleber, D., High performance liquid chromatographic resolution of the optical isomers of D,L-tryptophan, D,L-5-hydroxytryptophan and D,L-dopa on cellulose columns, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 3, 31, 1980.

12. Takayanagi, H., Hatano, O., Fujimura, K., and Ando, T., Ligand-exchange high-performance liquid chromatography of dialkyl sulfides, *Anal. Chem.*, 57, 1840, 1985.
13. Armstrong, D.W., U.S. Patent 4,539,399, 1985, assigned to Advanced Separation Technologies Inc., Whippany, NJ.
14. Armstrong, D.W. and Demond, W., Cyclodextrin bonded phases for the liquid chromatographic separation of optical, geometrical, and structural isomers, *J. Chromatogr. Sci.*, 22, 411, 1984.
15. Armstrong, D.W., Ward, T.J., Armstrong, R.D., and Beesley, T.J., Separation of drug stereoisomers by the formation of  $\beta$ -cyclodextrin inclusion complexes, *Science*, 232, 1132, 1986.
16. Armstrong, D.W., DeMond, W., and Czech, B.P., Separation of metallocene enantiomers by liquid chromatography: chiral recognition via cyclodextrin bonded phases, *Anal. Chem.*, 57, 481, 1985.
17. Armstrong, D.W., DeMond, W., Alak, A., Hinze, W.L., Riehl, T.E., and Bui, K.H., Liquid chromatographic separation of diastereomers and structural isomers on cyclodextrin-bonded phases, *Anal. Chem.*, 57, 234, 1985.
18. Weaver, D.E. and van Lier, R., Coupled  $\beta$ -cyclodextrin and reverse-phase high-performance liquid chromatography for assessing biphenyl hydroxylase activity in hepatic 9000g supernatant, *Anal. Biochem.*, 154, 590, 1986.
19. Armstrong, D.W., Optical isomer separation by liquid chromatography, *Anal. Chem.*, 59, 84A, 1987.
20. Chang, C.A., Wu, Q., and Tan, L., Normal-phase high-performance liquid chromatographic separations of positional isomers of substituted benzoic acids with amine and  $\beta$ -cyclodextrin bonded-phase columns, *J. Chromatogr.*, 361, 199, 1986.
21. Cline-Love, L. and Arunyanart, M., Cyclodextrin mobile-phase and stationary-phase liquid chromatography, *ACS Symp. Ser.*, 297, 226, 1986.
22. Feitsma, K., Bosman, J., Drenth, B., and DeZeeuw, R., A study of the separation of enantiomers of some aromatic carboxylic acids by high-performance liquid chromatography on a  $\beta$ -cyclodextrin-bonded stationary phase, *J. Chromatogr.*, 333, 59, 1985.
23. Fujimura, K., Ueda, T., and Ando, T., Retention behavior of some aromatic compounds on chemically bonded cyclodextrin silica stationary phase in liquid chromatography, *Anal. Chem.*, 55, 446, 1983.
24. Hattori, K., Takahashi, K., Mikami, M., and Watanabe, H., Novel high-performance liquid chromatographic adsorbents prepared by immobilization of modified cyclodextrins, *J. Chromatogr.*, 355, 383, 1986.
25. Ridlon, C.D. and Issaq, H.J., Effect of column type and experimental parameters on the HPLC separation of dipeptides, *J. Liq. Chromatogr.*, 9, 3377, 1986.
26. Sybilska, D., Debowski, J., Jurczak, J., and Zukowski, J., The  $\alpha$ - and  $\beta$ -cyclodextrin complexation as a tool for the separation of o-, m- and p-nitro-, cis- and trans-cinnamic acids by reversed-phase high-performance liquid chromatography, *J. Chromatogr.*, 286, 163, 1984.
27. Chang, C.A., Wu, Q., and Eastman, M.P., Mobile phase effects on the separations of substituted anilines with  $\alpha$ -cyclodextrin-bonded column, *J. Chromatogr.*, 371, 269, 1986.
28. Maguire, J.H., Some structural requirements for resolution of hydantoin enantiomers with  $\alpha$ -cyclodextrin liquid chromatography column, *J. Chromatogr.*, 387, 453, 1987.
29. Sinibaldi, M., Carunchio, V., Coradini, C., and Girelli, A.M., High-performance liquid chromatographic resolution of enantiomers on chiral amine bonded silica gel, *Chromatographia*, 18, 459, 1984.
30. Pettersson, C. and Stuurman, H.W., Direct separation of enantiomer of ephedrine and some analogues by reversed-phase liquid chromatography using (+)-di-n-butyltartrate as the liquid stationary phase, *J. Chromatogr. Sci.*, 22, 441, 1984.
31. Weems, H.B., Mushtaq, M., and Yang, S.K., Resolution of epoxide enantiomers of polycyclic aromatic hydrocarbons by chiral stationary-phase high-performance liquid chromatography, *Anal. Biochem.*, 148, 328, 1985.
32. Weems, H., Mushtaq, M., Fu, P., and Yang, S., Direct separation of non-k-region monool and diol enantiomers of phenanthrene, benz[a]anthracene, and chrysene by high-performance liquid chromatography with chiral stationary phases, *J. Chromatogr.*, 371, 211, 1986.
33. Yang, S., Mushtaq, M., and Fu, P., Elution order: absolute configuration of k-region dihydrodiol enantiomers of benz[a]anthracene derivatives in chiral stationary phase high performance liquid chromatography, *J. Chromatogr.*, 371, 195, 1986.
34. Wainer, I., Applicability of HPLC chiral stationary phases to pharmacokinetic and disposition studies on enantiomeric drugs, *Methodol. Serv. Biochem. Anal. Subser. A*, 16, 243, 1986.



35. Vaughan, G.T. and Milborrow, B.V., The resolution by HPLC of RS-[2-<sup>14</sup>C] Me 1',4'-cis-diol of abscisic acid and the metabolism of (–)-R- and S-abscisic acid, *J. Exp. Bot.*, 35, 110, 1984.
36. Tambute, A., Gareil, P., Caude, M., and Rosset, R., Preparative separation of racemic tertiary phosphine oxides by chiral high-performance liquid chromatography, *J. Chromatogr.*, 363, 81, 1986.
37. Wainer, I. and Doyle, T., The direct enantiomeric determination of (–) and (+)-propranolol in human serum by high-performance liquid chromatography on a chiral stationary phase, *J. Chromatogr.*, 306, 405, 1984.
38. Okamoto, Y., Mohri, H., Ishikura, M., Hatada, K., and Yuki, H., Optically active poly(diphenyl-2-pyridylmethyl methacrylate): asymmetric synthesis, stability of helix, and chiral recognition ability, *J. Polymer Sci. Polymer Symp.*, 74, 125, 1986.
39. Gubitz, G. and Mihellyes, S., Direct separation of 2-hydroxy acid enantiomers by high-performance liquid chromatography on chemically bonded chiral phases, *Chromatographia*, 19, 257, 1984.
40. Schulze, J. and Konig, W., Enantiomer separation by high-performance liquid chromatography on silica gel with covalently bound mono-saccharides, *J. Chromatogr.*, 355, 165, 1986.
41. Kip, J., Van Haperen, P., and Kraak, J.C., R-N-(pentafluorobenzoyl) phenylglycine as a chiral stationary phase for the separation of enantiomers by high-performance liquid chromatography, *J. Chromatogr.*, 356, 423, 1986.
42. Gelber, L.R., Karger, B.L., Neumeyer, J.L., and Feibush, B., Ligand exchange chromatography of amino alcohols: use of Schiff bases in enantiomer resolution, *J. Am. Chem. Soc.*, 106, 7729, 1984.
43. Dabashi, Y. and Hara, S., Direct resolution of enantiomers by liquid chromatography with the novel chiral stationary phase derived from (R,R)-tartramide, *Tetrahedron Lett.*, 26, 4217, 1985.
44. Facklam, C., Pracejus, H., Oehme, G., and Much, H., Resolution of enantiomers of amino acid derivatives by high-performance liquid chromatography in a silica gel bonded chiral amide phase, *J. Chromatogr.*, 257, 118, 1983.
45. Okamoto, Y., Honda, S., Hatada, K., and Yuki, H., IX. High-performance liquid chromatographic resolution of enantiomers on optically active poly(tri-phenylmethyl methacrylate), *J. Chromatogr.*, 350, 127, 1985.
46. Okamoto, Y. and Hatada, K., Resolution of enantiomers by HPLC on optically active poly(triphenylmethyl methacrylate), *J. Liq. Chromatogr.*, 9, 369, 1986.
47. Armstrong, D.W., Tang, Y., Chen, S., Zhou, C., Bagwill, J.R., and Chen, J.R., Macrocyclic antibiotics as a new class of chiral selectors for liquid chromatography, *Anal. Chem.*, 66, 1473, 1994.
48. Ekborg-Ott, K.H., Liu, Y., and Armstrong, D.W., Highly enantioselective HPLC separations using the covalently bonded macrocyclic antibiotic ristocetin A chiral stationary phase, *Chirality*, 10, 434, 1998.
49. Armstrong, D.W., Liu, Y., and Ekborg-Ott, K.H., A covalently bonded teicoplanin chiral stationary phase for HPLC enantioseparations, *Chirality*, 7, 474, 1995.
50. Berthod, A., Liu, Y., Bagwill, J.R., and Armstrong, D.W., Facile RPLC enantioresolution of native amino acids and peptides using a teicoplanin chiral stationary phase, *J. Chromatogr. A*, 731, 123, 1996.
51. Berthod, A., Chen, X., Kullman, J.P., Armstrong, D.W., Gasparrini, F., D'Acquarica, I., Villani, C., and Carotti, A., Role of carbohydrate moieties in chiral recognition on teicoplanin based LC stationary phases, *Anal. Chem.*, 72, 1736, 2000.
52. Aboul-Enein, H.Y. and Serignese, V., Enantiomeric separation of several cyclic imides on a macrocyclic antibiotic (vancomycin) chiral stationary phase under normal and reverse phase conditions, *Chirality*, 10, 358, 1998.
53. Lehotay, J., Hrobonova, J., Krupcik, J., and Cizmarik, J., Chiral separation of enantiomers of amino acid derivatives by HPLC on vancomycin and teichoplanin chiral stationary phases, *Pharmazie*, 53, 863, 1998.

## Chiral Stationary Phases for HPLC

**Name:** Bovine serum albumin (covalently fixed to silica gel)

**Structure:** Prolate ellipsoid  $14 \times 4$  nm, with a molecular mass of 66,500; amount absorbed is dependent on buffer pH, with the maximum at pH = 4.9

**Analytical Properties:** Separation of bopindolol and also separation of pindolol after derivatization with isopropyl isocyanate; separation of DL mixtures of enantiomers; can be used on both the analytical and preparative scales; changes in pH will cause this phase to leach from the column; storage at 4°C is recommended

**Reference:** 1, 2

**Name:**  $\alpha$ -Acid glycoprotein

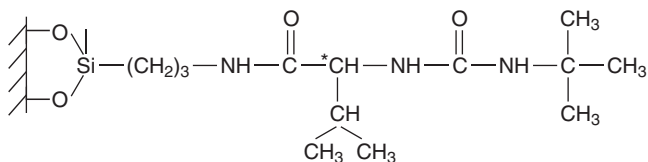
**Structure:** Structure is proprietary, Enantiopac, LKB Co.

**Analytical Properties:** Separation of the drugs ibuprofen, ketoprofen, naproxen, 2-phenoxypropionic acid, bendroflumethiazide, ethotoin, hexobarbital, disopyramide, and RAC 109; retention and selectivity of the solutes can be regulated by addition of the tertiary amine *N,N*-dimethyloctylamine (DMOA) to the mobile phase; DMOA decreases retention time and the enantioselectivity of the weaker acids but has opposite effects on the stronger acids

**Reference:** 3

**Name:** *N*-(*t*-Butylamino carbonyl-L-valine) bonded silica

**Structure:**

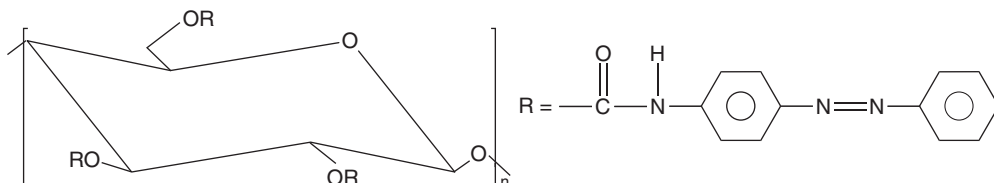


**Analytical Properties:** Separation of amino acid enantiomers; most effective of the L-valine urea derivatives; depends on hydrogen bond interactions usually prepared on LiChro-sorb (10  $\mu$ m); hexane plus isopropanol modifier has been used as the liquid phase

**Reference:** 4

**Name:** Cellulose *cis*- and *trans*-tris (4-phenylazophenyl carbamate) (CPAPC)

**Structure:**

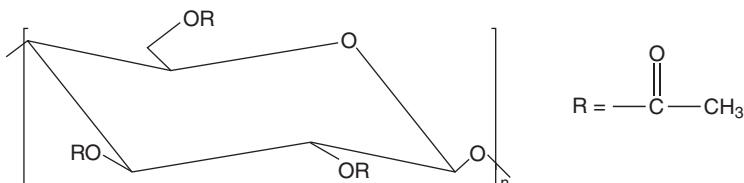


**Analytical Properties:** *Trans* isomer provides excellent resolution of racemic mixtures such as atropine, pindolol, flavanone; resolution decreases quickly with increasing *cis* isomer concentration; the *cis/trans* equilibrium is controlled by UV radiation, and the phase is adsorbed to silica gel; liquid phase of hexane with 10% 2-propanol has been found useful

**Reference:** 5

**Name:** Cellulose triacetate

**Structure:**



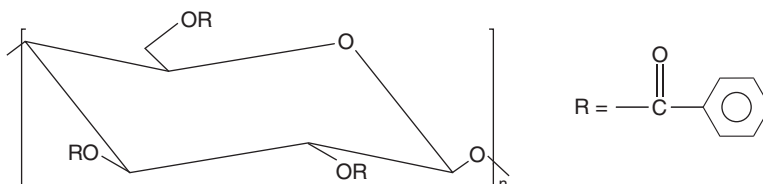
### Chiral Stationary Phases for HPLC (continued)

**Analytical Properties:** Shows chiral recognition for many racemates and is especially effective for substrates with a phosphorus atom at an asymmetric center; however, the degree of chiral recognition is not so high in general

**Reference:** 6

**Name:** Cellulose tribenzoate

**Structure:**

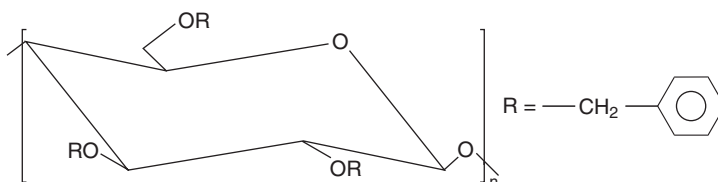


**Analytical Properties:** Demonstrates good chiral recognition for the racemates with carbonyl group(s) in the neighborhood of an asymmetric center

**Reference:** 6

**Name:** Cellulose tribenzyl ether

**Structure:**

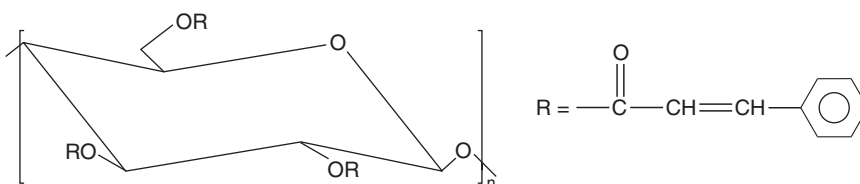


**Analytical Properties:** Effective with protic solvents used as mobile phases

**Reference:** 6

**Name:** Cellulose tricinnamate

**Structure:**

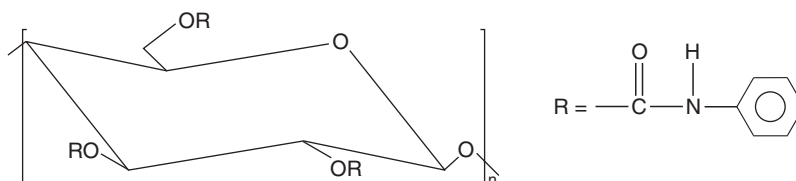


**Analytical Properties:** Shows high chromatographic retention times and a good chiral recognition for many aromatic racemates and barbiturates

**Reference:** 6

**Name:** Cellulose tris (phenylcarbamate)

**Structure:**



### Chiral Stationary Phases for HPLC (continued)

**Analytical Properties:** Separation of racemic mixtures of alkaloids, using ethanol as the eluent; 1-isomers tend to be more strongly retained than D-isomers; good chiral recognition of sulfoxides and high affinity for racemates having an –OH or –NH group, through hydrogen bonding

**Reference:** 6, 7

**Name:** Cross-linked acetylcellulose

**Structure:** Cellulose with one of the –OH groups acylated

**Analytical Properties:** Separation of enantiomers (such as etozolin, piprozolin, ozolinon, and bunolol) using an ethanol/water, 95/5 (v/v%) liquid phase

**Reference:** 8

**Name:** Microcrystalline tribenzoylcellulose

**Structure:** Same structure as cellulose trobenzoate (coated on macroporous silica gel)

**Analytical Properties:** Resolution of *trans*-1,2-diphenyloxirane, 2-methyl-3-(2'-methylphenyl)-4(3H)-quinazolinone, and some aromatic hydrocarbons

**Reference:** 9

**Name:** Triacetylcellulose

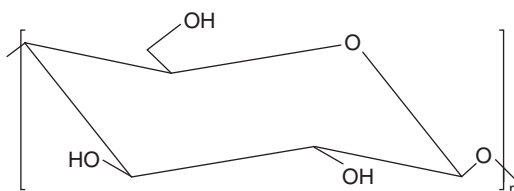
**Structure:** Same structure as cellulose triacetate

**Analytical Properties:** Microcrystalline triacetylcellulose swells in organic solvents; separation of racemic thioamides, sulfoxides, organophosphorus compounds, drugs, and amino acids derivatives; separations of these racemates were achieved at pressures at or above 4.9 MPa

**Reference:** 10

**Name:** Untreated cellulose (average particle size of 7  $\mu\text{m}$ )

**Structure:**

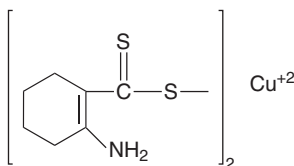


**Analytical Properties:** Complete resolution of D,L-tryptophane and D,L-5-hydroxytryptophane

**Reference:** 11

**Name:** Copper (II) 2-amino-1-cyclopentene-1-dithiocarboxylate

**Structure:**



(bonded to silica)

**Analytical Properties:** Separation of dialkyl sulfides when hexane containing methanol or acetonitrile was used as the mobile phase

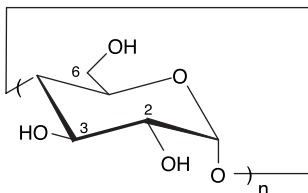
**Reference:** 12

### Chiral Stationary Phases for HPLC (continued)

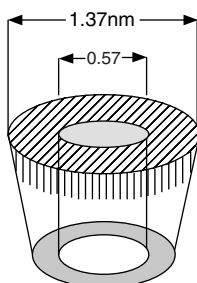
**Name:**  $\alpha$ -Cyclodextrin bonded phase

**Structure:**

Subunit:



Cavity:



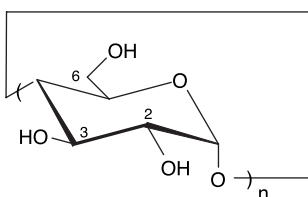
**Analytical Properties:**  $\alpha$ -Cyclodextrin (cyclohexamolyose); reverse phase separation of barbiturates and other drugs, and aromatic amino acids; the substrate is composed of six glucose units and has a relative molecular mass of 972; the cavity diameter is 0.57 nm, and the substrate has a water solubility of 14.5 g/ml

**Reference:** 13–28

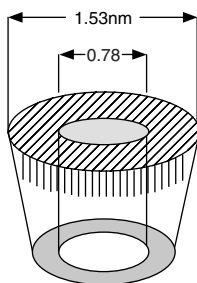
**Name:**  $\beta$ -Cyclodextrin bonded phase

**Structure:**

Subunit:

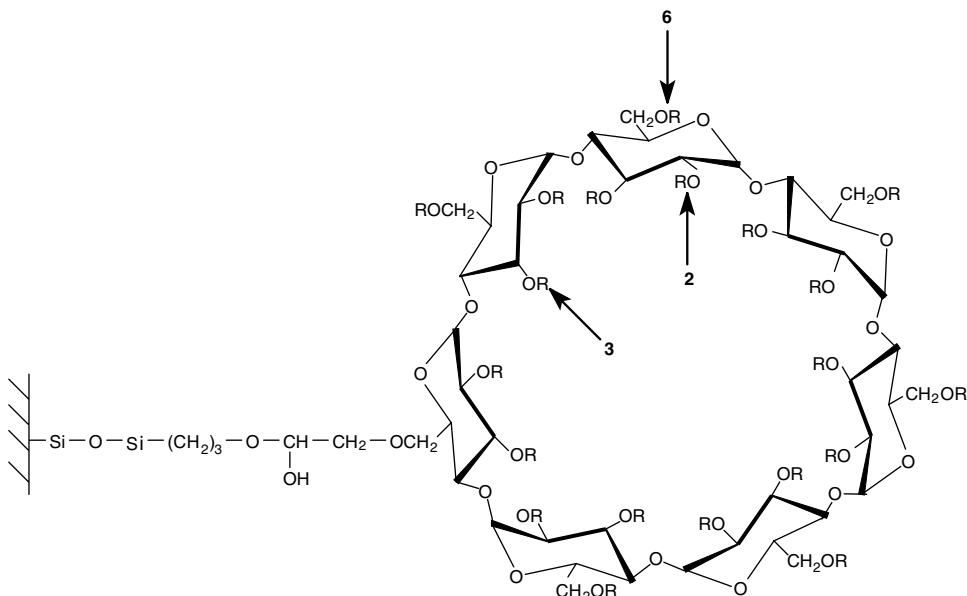


Cavity:



## Chiral Stationary Phases for HPLC (continued)

Ligand:



Note that this structure also illustrates the linkage to silica through one primary  $\text{-OH}$  group. Either one or two such linkages usually attach the substrate to the silica. The numbers (2, 3, and 6) indicate the three points on each of the subunits where subsequent phase modification can take place.

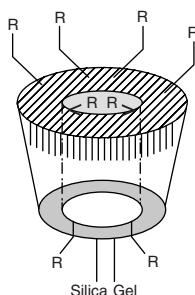
**Analytical Properties:**  $\beta$ -Cyclodextrin (cycloheptamylose); normal phase separation of positional isomers of substituted benzoic acids; reverse phase separation of dansyl and naphthyl amino acids, several aromatic drugs, steroids, alkaloids, metallocenes, binaphthyl crown ethers, aromatics acids, aromatic amines, and aromatic sulfoxides; this substrate has seven glucose units and has a relative molecular mass of 1135; the inside cavity has a diameter of 0.78 nm, and the substrate has a water solubility of 1.85 g/ml, although this can be increased by derivatization

**Reference:** 13–28

**Name:**  $\beta$ -Cyclodextrin, dimethylated bonded phase

**Structure:**

Cavity:



R-ligand:



**Analytical Properties:**  $\beta$ -Cyclodextrin DM (cycloheptamylose-DM); reverse phase separation of a variety of structural and geometrical isomers; useful for the separation of analytes that have a carbonyl group off of the stereogenic center

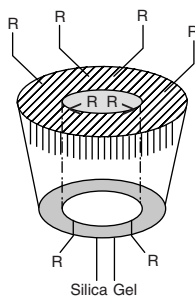
**Reference:** 13–28

### Chiral Stationary Phases for HPLC (continued)

**Name:**  $\beta$ -Cyclodextrin, acetylated bonded phase

**Structure:**

Cavity:



R-ligand:



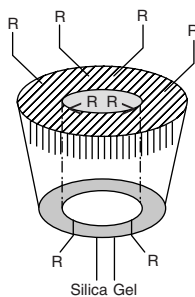
**Analytical Properties:**  $\beta$ -Cyclodextrin AC (cycloheptamylose-AC); reverse phase separation of steroids and polycyclic compounds

**Reference:** 13–28

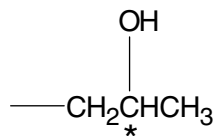
**Name:**  $\beta$ -Cyclodextrin, hydroxypropyl ether modified bonded phase

**Structure:**

Cavity:



R-ligand:



**Analytical Properties:**  $\beta$ -Cyclodextrin SP or RSP (cycloheptamylose-SP, -RSP); note that the modifying ligand has a stereogenic center; useful for reverse phase separation of a variety of analytes, especially for enantiomers that have bulky substituents that are beta to the stereogenic center; can be used for cyclic hydrocarbons and for t-boc amino acids

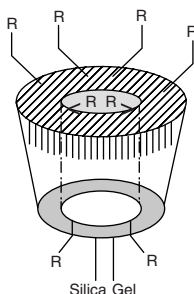
**Reference:** 13–28

### Chiral Stationary Phases for HPLC (continued)

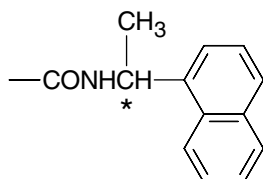
**Name:**  $\beta$ -Cyclodextrin, naphthylethyl carbamate modified bonded phase

**Structure:**

Cavity:



R-ligand:



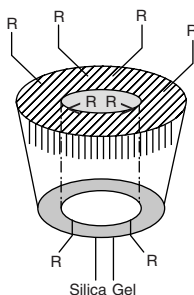
**Analytical Properties:**  $\beta$ -Cyclodextrin SN or RN (cycloheptamylose-SN, -RN); note that the modifying ligand has a stereogenic center; useful for normal phase, reverse phase, and polar organic phase separation under specific circumstances; the substrate performs best with normal phase and polar organic mobile phases; the SN modification has shown the highest selectivity

**Reference:** 13–28

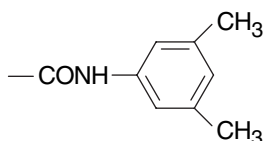
**Name:**  $\beta$ -Cyclodextrin, 3,5-dimethylphenyl carbamate modified bonded phase

**Structure:**

Cavity:



R-ligand:



**Analytical Properties:**  $\beta$ -Cyclodextrin DMP (cycloheptamylose-DMP); useful for normal phase, reverse phase, and polar organic phase separation under specific circumstances; the substrate performs best with normal phase and polar organic mobile phases

**Reference:** 13–28

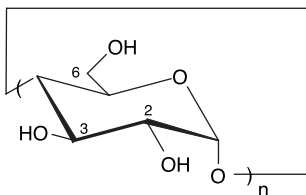


## Chiral Stationary Phases for HPLC (continued)

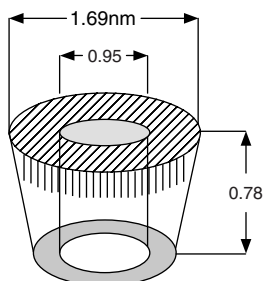
**Name:**  $\gamma$ -Cyclodextrin bonded phase

**Structure:**

Subunit:



Cavity:

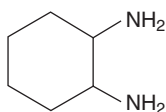


**Analytical Properties:**  $\gamma$ -Cyclodextrin (cyclooctylamalyose), reverse phase separation of stereoisomers of polycyclic aromatic hydrocarbons; the substrate has eight glucose units and has a relative molecular mass of 1297; the cavity has a diameter of 0.59 nm, and the substrate has a water solubility of 23.2 g/ml

**Reference:** 13–28

**Name:** (–) *Trans*-1,2-cyclohexanediamine

**Structure:**



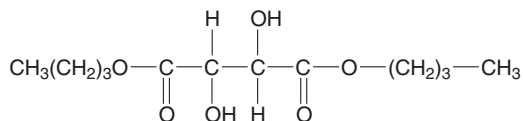
(bonded to silica gel)

**Analytical Properties:** Resolution of such enantiomeric compounds as 2,2'-dihydroxy-1,1'-binaphthyl and *trans*-1,2-cyclohexandiol

**Reference:** 29

**Name:** (+)-Di-*n*-butyltartrate

**Structure:**



(adsorbed on phenyl bonded silica)

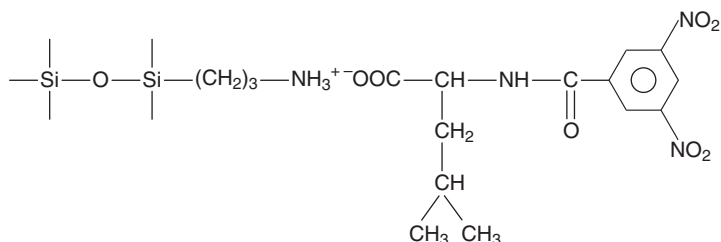
**Analytical Properties:** Resolution of ephedrine and nonephedrine

**Reference:** 30

### Chiral Stationary Phases for HPLC (continued)

**Name:** (*S*)-*N*-(3,5-Dinitrobenzoyl) leucine or (*S*)-DNBL

**Structure:**

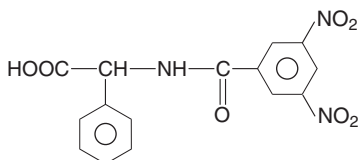


**Analytical Properties:** Resolution of several enantiomers of polycyclic aromatic hydrocarbons, for example, chrysene 5,6-epoxide, dibenz[a,h]anthracene 5,6-epoxide, 7-methyl benz[a]anthracene 5,6-epoxide; resolution of barbiturates, mephentyoin, benzodiazepinones, and succinimides; direct separation of some mono-ol and diol enantiomers of phenanthrene, benz[a]anthrene, and chrysene; ionically bonded to silica gel, this phase provides resolution of enantiomers of *cis*-dihydrodiols of unsubstituted and methyl- and bromo-substituted benz[a]anthracene derivatives having hydroxyl groups that adopt quasiequatorial-quasial axial and quasial axial-quasiequatorial conformation

**Reference:** 31–35

**Name:** (*R*)-*N*-(3,5-Dinitrobenzyl) phenylglycine

**Structure:**

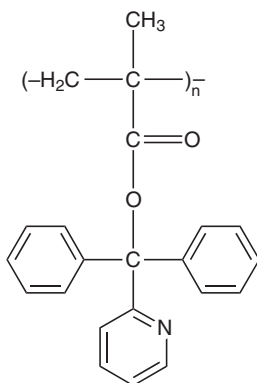


**Analytical Properties:** Ionically bonded to silica, this phase provides good resolution of enantiomeric quasiequatorial *trans*-dehydrodiols of unsubstituted and methyl- and bromo-substituted benz[a]anthracene derivatives; covalently bonded to silica, this phase provides good resolution of enantiomeric pairs of quasidial axial *trans*-dihydrodiols of unsubstituted and methyl- and bromo-substituted benz[a]anthracene derivatives; by addition of a third solvent (chloroform) to the classical binary mixture (hexane-alcohol) of the mobile phase, resolution of enantiomers of tertiary phosphine oxides is possible

**Reference:** 31–33, 36, 37

**Name:** Poly(diphenyl-2-pyridylmethyl methacrylate) or PD2PyMa

**Structure:**



(coated on macroporous silica gel)

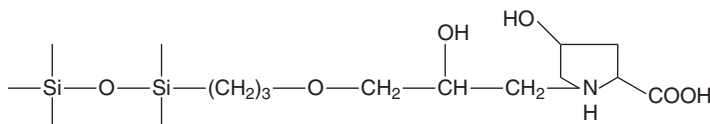
### Chiral Stationary Phases for HPLC (continued)

**Analytical Properties:** Resolution of such compounds as racemic 1,2-diphenol-ethanol, 2,2'-dihydroxyl-1,1'-dinaphthyl, 2,3-diphenyloxirane, and phenyl-2-pyrid- $\alpha$ -tolyl-1-methanol

**Reference:** 38

**Name:** L-Hydroxyproline

**Structure:**



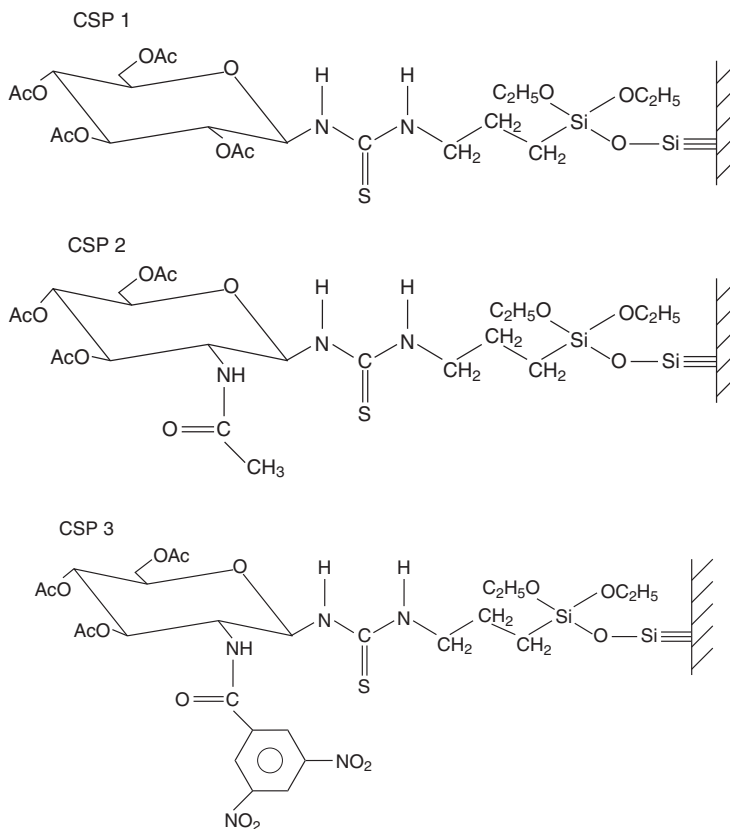
(as a fixed ligand on a silica gel; Cu (II) used as complexing agent)

**Analytical Properties:** Chiral phases containing L-hydroxyproline as a fixed ligand show high enantio-selectivity for 2-hydroxy acids; these phases have resolved some aromatic as well as aliphatic 2-hydroxy acids

**Reference:** 39

**Name:** 1-Isothiocyanato-D-glucopyranosides

**Structure:**



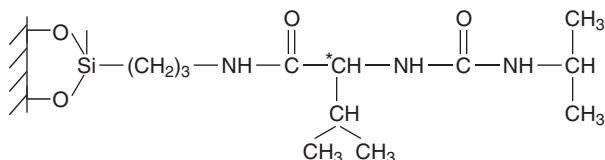
**Analytical Properties:** CSP (chiral stationary phase) 1 — separates some chiral binaphthyl derivatives when mixtures of hexane diethyl ether, dichloromethane, or dioxane are used as the mobile phase; CSP 2 — separates compounds with carbamate or amide functions (mixtures of *n*-hexane and 2-propanol can be used as mobile phase); CSP 3 — separation of compounds separated by CSP 2, as well as separation of compounds with carbonyl or amide functions and some amino alcohols that have pharmaceutical relevance ( $\beta$ -blockers)

**Reference:** 40

## Chiral Stationary Phases for HPLC (continued)

**Name:** *N*-Isopropylamino carbonyl-L-valine bonded silica

**Structure:**

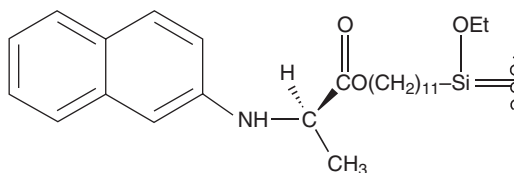


**Analytical Properties:** Separation of amino acid enantiomers; good chiral recognition of *N*-acetyl amino acid methyl esters; depends on hydrogen bond interactions; hexane with isopropanol modifier has been used as the liquid phase; usually prepared on LiChrosorb (10 μm)

**Reference:** 4

**Name:** (*R*)- or (*S*)-*N*-(2-Naphthyl) alanine

**Structure:**



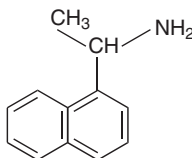
(*R*)-*N*-(2-naphthyl)-alanine

**Analytical Properties:** High selectivities for a variety of dinitrobenzoyl derivatized compounds

**Reference:** 19

**Name:** (*S*)-1-(α-Naphthyl) ethylamine

**Structure:**

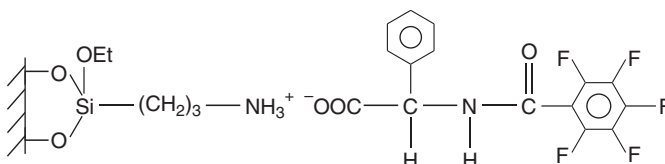


**Analytical Properties:** Separation of 3,5-dinitrobenzoyl derivatives of amino acids; 3,5-dinitroanilide derivatives of carboxylic acids

**Reference:** 19

**Name:** *R*-*N*-(Pentafluorobenzoyl) phenylglycine

**Structure:**

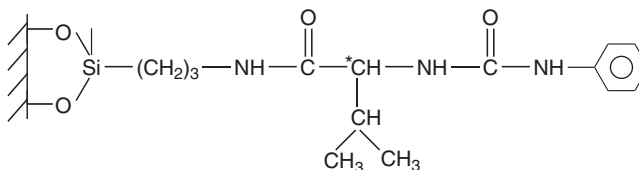


### Chiral Stationary Phases for HPLC (continued)

**Analytical Properties:** Higher selectivity for nitrogen-containing racemates than *R-N*-(3,5-dinitrobenzoyl) phenylglycine; examples of nitrogen-containing racemates include succinimides, hydantoins, and mandelates  
**Reference:** 41

**Name:** *N*-Phenylaminocarbonyl-L-valine bonded silica

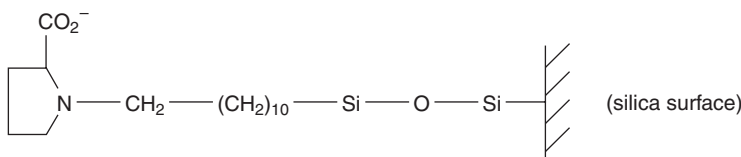
**Structure:**



**Analytical Properties:** Separation of amino acid enantiomers by hydrogen bond interactions; usually prepared on LiCrosorb (10  $\mu\text{m}$ ); hexane plus isopropanol modifier commonly used as liquid phase  
**Reference:** 4

**Name:** (L-Proline) copper (II)

**Structure:**

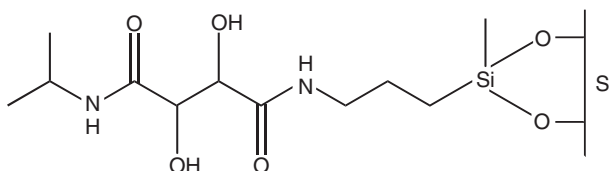


**Analytical Properties:** Separation of primary  $\alpha$ -amino alcohols, for example,  $\beta$ -hydroxyphenethylamines and catecholamines

**Reference:** 42

**Name:** Derivative of (R,R)-tartramide

**Structure:**

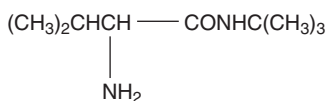


**Analytical Properties:** Resolution of a series of  $\beta$ -hydroxycarboxylic acids as *t*-butylamide derivatives

**Reference:** 43

**Name:** *t*-butylvalinamide

**Structure:**



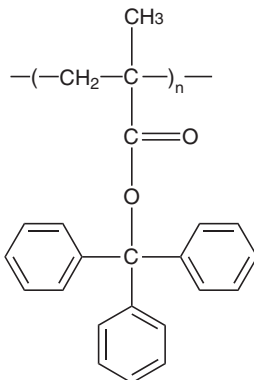
**Analytical Properties:** Resolution of heavier amino acid derivatives

**Reference:** 44

### Chiral Stationary Phases for HPLC (continued)

**Name:** (+)-Poly(triphenylmethyl methacrylate) or (+)-PTMA

**Structure:**

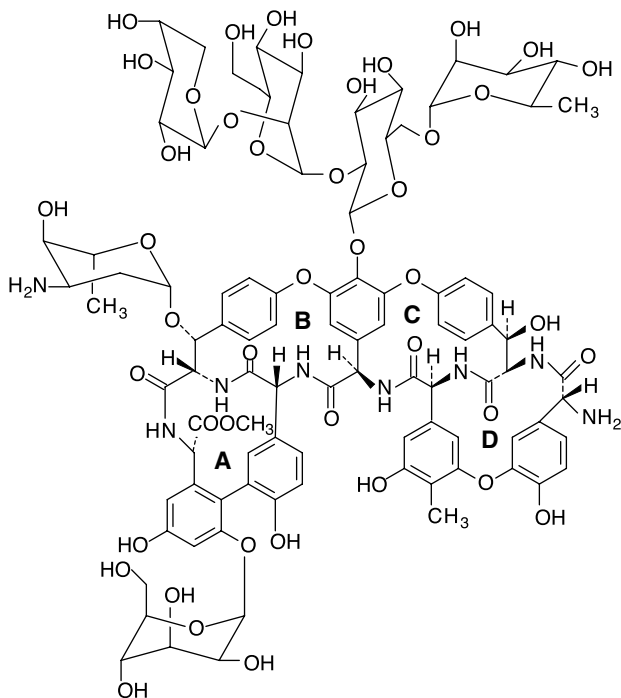


**Analytical Properties:** Resolution of enantiomers such as *trans*-1,3-cyclohexene dibenzoate, 3,5-pentylene dibenzoate, 3,5-dichlorobenzoate, triacetylacetates, and racemic compounds having phosphorus as a chiral center; this phase will also resolve achiral compounds

**Reference:** 45, 46

**Name:** Ristocetin-A bonded phase

**Structure:**



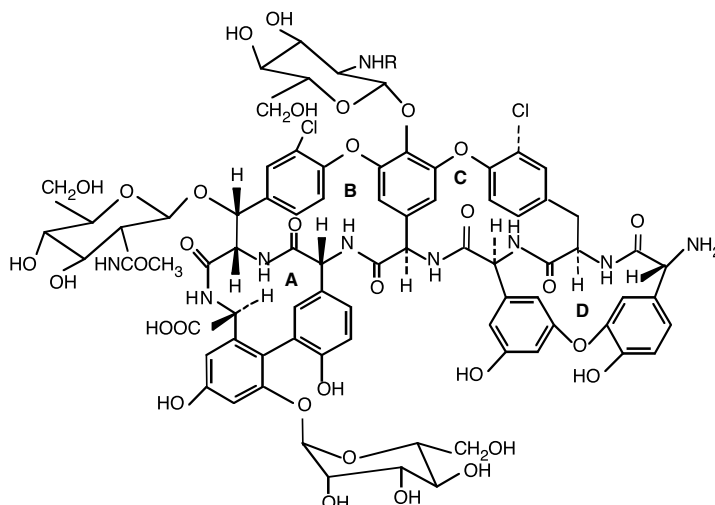
**Analytical Properties:** Substrate has 38 chiral centers and 7 aromatic rings surrounding 4 cavities (A, B, C, D), making this the most structurally complex of the macrocyclic glycopeptides; substrate has a relative molecular mass of 2066; this phase can be used in normal, reverse, and polar organic phase separations; selective for anionic chiral species; with polar organic mobile phases, it can be used for  $\alpha$ -hydroxy acids, profens, and N-blocked amino acids; in normal phase mode, it can be used for imides, hydantoins, and N-blocked amino acids; in reverse phase, it can be used for  $\alpha$ -hydroxy and halogenated acids, substituted aliphatic acids, profens, N-blocked amino acids, hydantoins, and peptides

**Reference:** 47, 48

### Chiral Stationary Phases for HPLC (continued)

**Name:** Teicoplanin bonded phase

**Structure:**

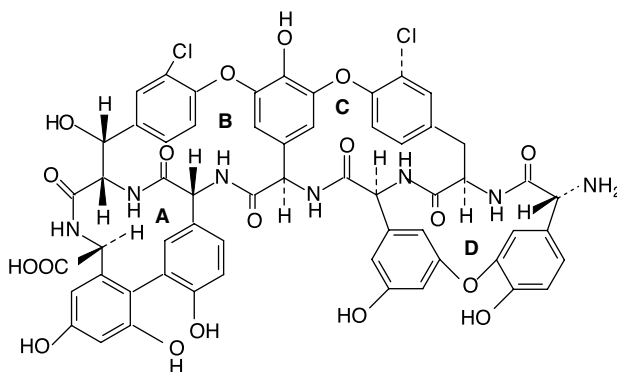


**Analytical Properties:** Substrate has 20 chiral centers and 7 aromatic rings surrounding 4 cavities (A, B, C, D); substrate has a relative molecular mass of 1885; separation occurs through chiral hydrogen bonding sites,  $\pi$ - $\pi$  interactions, and inclusion complexation in polar organic, normal, and reverse mobile phases; useful for the resolution of  $\alpha$ ,  $\beta$ , and  $\gamma$  or cyclic amino acids, small peptides, and N-derivatized amino acids

**Reference:** 49, 50

**Name:** Teicoplanin aglycone bonded phase

**Structure:**



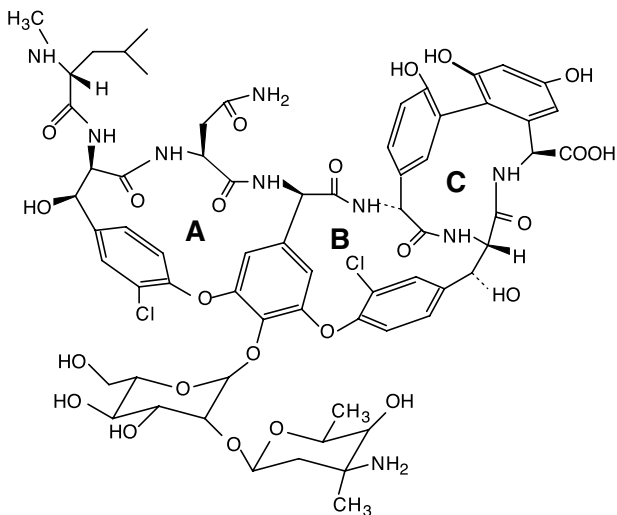
**Analytical Properties:** Substrate has eight chiral centers and seven aromatic rings surrounding four cavities (A, B, C, D); substrate has a relative molecular mass of 1197; separation occurs through chiral hydrogen bonding sites,  $\pi$ - $\pi$  interactions, and inclusion complexation in polar organic, normal, and reverse mobile phases; highly selective for amino acids ( $\alpha$ ,  $\beta$ , and  $\gamma$  or cyclic), some N-blocked amines, many neutral cyclic compounds, peptides, diazepines, hydantoins, oxazolidinones, and sulfoxides

**Reference:** 51

### Chiral Stationary Phases for HPLC (continued)

**Name:** Vancomycin bonded phase

**Structure:**



**Analytical Properties:** Substrate has 18 chiral centers and 5 aromatic rings surrounding 3 cavities (A, B, C); substrate has a relative molecular mass of 1449 and an isoelectric point of 7.2, with pKs of 2.9, 7.2, 8.6, 9.6, 10.4, and 11.7; separation occurs through chiral hydrogen bonding sites,  $\pi$ - $\pi$  interactions, a peptide binding site, and inclusion complexation in polar organic, normal, and reverse mobile phases; selective for cyclic amines, amides, acids, esters, and neutral molecules; high sample capacity

**Reference:** 52, 53



## DETECTORS FOR LIQUID CHROMATOGRAPHY

The following table provides some comparative data for the selection and operation of the more common detectors applied to high-performance liquid chromatography.<sup>1-5</sup> In general, the operational parameters provided are for optimized systems and represent the maximum obtainable in terms of sensitivity and linearity. In this table, the molar extinction coefficient is represented by  $\epsilon$ .

### REFERENCES

1. Pryde, A. and Gilbert, M.T., *Applications of High Performance Liquid Chromatography*, Chapman & Hall, London, 1979.
2. Hamilton, R.J. and Sewell, P.A., *Introduction to High Performance Liquid Chromatography*, Chapman & Hall, London, 1977.
3. Ahuja, S., *Trace and Ultratrace Analysis by HPLC*, Chemical Analysis Series, John Wiley & Sons, New York, 1991.
4. Snyder, L.R., Kirkland, J.J., and Glajch, J., *Practical HPLC Method Development*, John Wiley & Sons, New York, 1997.
5. Bruno, T.J., A review of hyphenated chromatographic instrumentation, *Sep. Purif. Methods*, 29, 63, 2000.

### Detectors for Liquid Chromatography

Detector	Sensitivity	Linearity	Selectivity	Comments
Ultraviolet spectrophotometer	$1 \times 10^{-9}$ g (for compounds of $\epsilon = 10,000\text{--}20,000$ )	$1 \times 10^4$	For UV-active functionalities, on the basis of absorptivity	Relatively insensitive to flow and temperature fluctuations; nondestructive, useful with gradient elution; use mercury lamp for 254 nm and quartz–iodine lamp for 350–700 nm; often a diode-array instrument is used to obtain entire UV–vis. spectrum
Refractive index detector (RID)	$1 \times 10^{-7}$ g	$1 \times 10^4$	Universal, dependent on refractive index difference with mobile phase	Relatively insensitive to flow fluctuations, but sensitive to temperature fluctuations; nondestructive, cannot be used with gradient elution; solvents must be degassed to avoid bubble formations; laser-based RI detectors offer higher sensitivity
Fluorometric detector	$1 \times 10^{-11}$ g	$1 \times 10^5$	For fluorescent species with conjugated bonding and aromaticity	Relatively insensitive to temperature and flow fluctuations; nondestructive; can be used with gradient elution; often, chemical derivatization is done on analytes to form fluorescent species; uses deuterium lamp for 190–400 nm or tungsten lamp for 350–600 nm
Electrochemical detectors Amperometric	$1 \times 10^{-9}$ g	$2 \times 10^4$	Responds to –OH functionalities	Used for aliphatic and aromatic –OH compounds, amines, and indoles; pulsed potential units are most sensitive, can be used with gradient elution and organic mobile phases; senses compounds in oxidative or reductive modes; mobile phases must be highly pure and purged of $O_2$
Conductivity detector	$1 \times 10^{-9}$ g		Specific to ionizable compounds	Uses postcolumn derivatization to produce ionic species; especially useful for certain halogen, sulfur, and nitrogen compounds
Mass spectrometers	Interface dependent	Interface dependent	Universal, within limits imposed by interface	Complex, expensive devices highly dependent on an efficient interface; electrospray and thermospray interfaces are most common; linear response is difficult to achieve

## ULTRAVIOLET DETECTION OF CHROMOPHORIC GROUPS

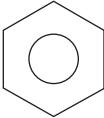
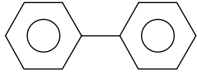
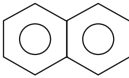
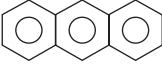

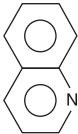
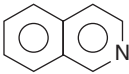
The following table is provided to aid in the use of applications of ultraviolet spectrophotometric detectors. The data here are used to evaluate the potential of detection of individual chromophoric moieties on analytes.<sup>1-3</sup>

### REFERENCES

1. Willard, H.H, Dean, J.A., Settle, F.A., and Merritt, L.L., *Instrumental Methods of Analysis*, 7th ed., Wadsworth Publishing Co., Belmont, CA, 1995.
2. Silverstein, R.M. and Webster, F.X., *Spectrometric Identification of Organic Compounds*, 6th ed., John Wiley & Sons, New York, 1997.
3. Lambert, J.B., Shuruell, H.F., Verbit, L., Cooks, R.G., and Stout, G.H., *Organic Structural Analysis*, MacMillan Publishing Co., New York, 1976.

### Ultraviolet Detection of Chromophoric Groups

Chromophor	Functional Group	$\lambda_{\text{max}}$ , nm	$\epsilon_{\text{max}}$	$\lambda_{\text{max}}$ , nm	$\epsilon_{\text{max}}$	$\lambda_{\text{max}}$ , nm	$\epsilon_{\text{max}}$
Ether	—O—	185	1000				
Thioether	—S—	194	4600	215	1600		
Amine	—NH <sub>2</sub> —	195	2800				
Amide	—CONH <sub>2</sub>	<210	—				
Thiol	—SH	195	1400				
Disulfide	—S—S—	194	5500	255	400		
Bromide	—Br	208	300				
Iodide	—I	260	400				
Nitrile	—C≡N	160	—				
Acetylide (alkyne)	—C≡C—	175–180	6000				
Sulfone	—SO <sub>2</sub> —	180	—				
Oxime	—NOH	190	5000				
Azido	>C=N—	190	5000				
Alkene	>C=C<	190	8000				
Ketone	>C=O	195	1000	270–285	18–30		
Thioketone	>C=S	205	Strong				
Esters	—COOR	205	50				
Aldehyde	—CHO	210	Strong	280–300	11–18		
Carboxyl	—COOH	200–210	50–70				
Sulfoxide	>S → O	210	1500				
Nitro	—NO <sub>2</sub>	210	Strong				
Nitrite	—ONO	220–230	1000–2000	300–4000	10		
Azo	—N=N—	285–400	3–25				
Nitroso	—N=O	302	100				
Nitrate	—ONO <sub>2</sub>	270 (shoulder)	12				
Conjugated hydrocarbon	—(C=C) <sub>2</sub> — (acyclic)	210–230	21,000				
Conjugated hydrocarbon	—(C=C) <sub>3</sub> —	260	35,000				
Conjugated hydrocarbon	—(C=C) <sub>4</sub> —	300	52,000				
Conjugated hydrocarbon	—(C=C) <sub>5</sub> —	330	118,000				
Conjugated hydrocarbon	—(C=C) <sub>2</sub> — (alicyclic)	230–260	3000–8000				
Conjugated hydrocarbon	C=C—C≡C	219	6500				
Conjugated system	C=C—C=N	220	23,000				
Conjugated system	C=C—C=O	210–250	10,000–20,000			300–350	Weak
Conjugated system	C=C—NO <sub>2</sub>	229	9500				

Benzene		184	46,700	202	6900	255	170
Diphenyl				246	20,000		
Naphthalene		220	112,000	275	5600	312	175
Anthracene		252	199,000	375	7900		
Pyridine		174	80,000	195	6000	251	1700
Quinoline		227	37,000	270	3600	314	2750
Isoquinoline		218	80,000	266	4000	317	3500

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*Note:*  $\phi$  denotes a phenyl group.

## DERIVATIZING REAGENTS FOR HPLC

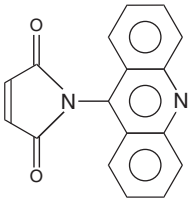
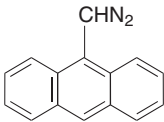
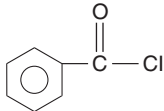
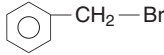
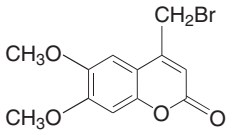
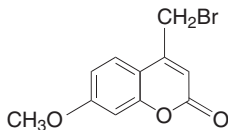
The following table provides a listing of the common reagents used in HPLC. Most of these reagents are used to impart a chromophoric or fluorescent group in the sample to enhance the detectability. Occasionally, a derivatization procedure is done in order to enhance selectivity, but this is the exception.

## REFERENCES

1. Umagat, H., Kucera, P., and Wen, L.-F., Total amino acid analysis using pre-column fluorescence derivatization, *J. Chromatogr.*, 239, 463, 1982.
2. Nimura, N. and Kinoshita, T., Fluorescent labeling of fatty acids with 9-anthryldiazomethane (ADAM) for high performance liquid chromatography, *Anal. Lett.*, 13, 191, 1980.
3. Lehrfeld, J., Separation of some perbenzoylated carbohydrates by high performance liquid chromatography, *J. Chromatogr.*, 120, 141, 1976.
4. Durst, H.D., Milano, M., Kikta, E.J., Connolly, S.A., and Grushka, E., Phenacyl esters of fatty acids via crown ether catalysts for enhanced ultraviolet detection in liquid chromatography, *Anal. Chem.*, 47, 1797, 1975.
5. Farinotti, R., Siard, Ph., Bourson, J., Kirkiacharian, S., Valeur, B., and Mohuzier, G., 4-Bromomethyl-6,7-dimethoxycoumarin as a fluorescent label for carboxylic-acids in chromatographic detection, *J. Chromatogr.*, 269, 81, 1983.
6. Lam, S. and Grushka, E., Labeling of fatty acids with 4-bromomethyl-7-methoxycoumarin via crown ether catalyst for fluorimetric detection in high-performance liquid chromatography, *J. Chromatogr.*, 158, 207, 1978.
7. Korte, W.D., 9-(Chloromethyl) anthracene: a useful derivatizing reagent for enhanced ultraviolet and fluorescence detection of carboxylic acids with liquid chromatography, *J. Chromatogr.*, 243, 153, 1982.
8. Ahnoff, M., Grundevik, I., Arfwidsson, A., Fonselius, J., and Persson, B.-A., Derivatization with 4-chloro-7-nitrobenzofurazan for liquid chromatographic determination of hydroxyproline in collagen hydrolysate, *Anal. Chem.*, 53, 485, 1981.
9. Linder, W., N-Chloromethyl-4-nitro-phthalimide as a derivatizing reagent for HPLC, *J. Chromatogr.*, 198, 367, 1980.
10. Lawrence, J.F., *Organic Trace Analysis by Liquid Chromatography*, Academic Press, New York, 1981.
11. Avigad, G., Dansyl hydrazine as a fluorimetric reagent for thin-layer chromatographic analysis of reducing sugars, *J. Chromatogr.*, 139, 343, 1977.
12. Lloyd, J.B.F., Phenanthramidazoles as fluorescent derivatives in the analysis of fatty acids by high-performance liquid chromatography, *J. Chromatogr.*, 189, 359, 1980.
13. Frei, R.W. and Lawrence, J.F., Eds., *Chemical Derivatization in Analytical Chemistry*, Vol. 1, Plenum Press, New York, 1981.
14. Goto, J., Komatsu, S., Goto, N., and Nambara, T., A new sensitive derivatization reagent for liquid chromatographic separation of hydroxyl compounds, *Chem. Pharm. Bull.*, 29, 899, 1981.
15. Musson, D.G. and Sternson, L.A., Conversion of arylhydroxylamines to electrochemically active derivatives suitable for high-performance liquid chromatographic analysis with amperometric detection, *J. Chromatogr.*, 188, 159, 1980.
16. Lankmayr, E.P., Budna, K.W., Müller, K., Nachtmann, F., and Rainer, F., Determination of d-penicillamine in serum by fluorescence derivatization and liquid column chromatography, *J. Chromatogr.*, 222, 249, 1981.
17. Mopper, K., Stahovec, W.L., and Johnson, L., Trace analysis of aldehydes by reversed-phase high-performance liquid chromatography and precolumn fluorogenic labeling with 5,5-dimethyl-1,3-cyclohexanedione, *J. Chromatogr.*, 256, 243, 1983.
18. Lawrence, J.F. and Frei, R.W., *Chemical Derivatization in Liquid Chromatography*, Elsevier, Amsterdam, 1976.

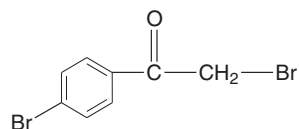
19. Carey, M.A. and Persinger, H.E., Liquid chromatographic determination of traces of aliphatic carbonyl compounds and glycols as derivatives that contain the dinitrophenyl group, *J. Chromatogr. Sci.*, 10, 537, 1972.
20. Fitzpatrick, F.A., Siggia, S., and Dingman, J., Sr., High speed liquid chromatography of derivatized urinary 17-keto steroids, *Anal. Chem.*, 44, 2211, 1972.
21. Pietrzyk, D.J. and Chan, E.P., Determination of carbonyl compounds by 2-diphenylacetyl-1,3-indandione-1-hydrazone, *Anal. Chem.*, 42, 37, 1970.
22. Braun, R.A. and Mosher, W.A., 2-Diphenylacetyl-1,3-indandione 1-hydrazone: a new reagent for carbonyl compounds, *J. Am. Chem. Soc.*, 80, 3048, 1958.
23. Schäfer, M. and Mutschler, E., Fluorimetric determination of oxprenolol in plasma by direct evaluation of thin-layer chromatograms, *J. Chromatogr.*, 164, 247, 1979.
24. Moye, H.A. and Boning, A.J., Jr., A versatile fluorogenic labelling reagent for primary and secondary amines: 9-fluorenylmethyl chloroformate, *Anal. Lett.*, 12, 25, 1979.
25. Lehninger, A.L., *Biochemistry*, 2nd ed., Worth Publishers, New York, 1978.
26. Roos, R.W., Determination of conjugated and esterified estrogens in pharmaceutical tablet dosage forms by high-pressure, normal-phase partition chromatography, *J. Chromatogr. Sci.*, 14, 505, 1976.
27. DeLeenheer, A., Sinsheimer, J.E., and Burckhalter, J.H., Fluorometric determination of primary and secondary aliphatic amines by reaction with 9-isothiocyanatoacridine, *J. Pharm. Sci.*, 62, 1370, 1973.
28. Clark, C.R. and Wells, M.M., Precolumn derivatization of amines for enhanced detectability in liquid chromatography, *J. Chromatogr. Sci.*, 16, 332, 1978.
29. Hulshoff, A., Roseboom, H., and Renema, J., Improved detectability of barbiturates in high-performance liquid chromatography by pre-column labelling and ultraviolet detection, *J. Chromatogr.*, 186, 535, 1979.
30. Matthees, D.P. and Purdy, W.C., Naphthylidiazomethane as a derivatizing agent for the high-performance liquid chromatography detection of bile acids, *Anal. Chim. Acta*, 109, 161, 1979.
31. Kuwata, K., Uebori, M., and Yamazaki, Y., Determination of phenol in polluted air as p-nitrobenzeneazophenol derivative by reversed phase high performance liquid chromatography, *Anal. Chem.*, 52, 857, 1980.
32. Nachtmann, F., Spitz, H., and Frei, R.W., Rapid and sensitive high-resolution procedure for digitalis glycoside analysis by derivatization liquid chromatography, *J. Chromatogr.*, 122, 293, 1976.
33. Knapp, D.R. and Krueger, S., Use of o-p-nitrobenzyl-N,N-diisopropylisourea as a chromogenic reagent for liquid chromatographic analysis of carboxylic acids, *Anal. Lett.*, 8, 603, 1975.
34. Jupille, T., UV-Visible absorption derivatization in liquid chromatography, *J. Chromatogr. Sci.*, 17, 160, 1979.
35. Dunlap, K.L., Sandridge, R.L., and Keller, J., Determination of isocyanates in working atmospheres by high speed liquid chromatography, *Anal. Chem.*, 48, 497, 1976.
36. Politzer, I.R., Griffin, G.W., Dowty, B.J., and Laseter, J.L., Enhancement of ultraviolet detectability of fatty acids for purposes of liquid chromatographic-mass spectrometric analyses, *Anal. Lett.*, 6, 539, 1973.
37. Cox, G.B., Estimation of volatile N-nitrosamines by high-performance liquid chromatography, *J. Chromatogr.*, 83, 471, 1973.
38. Borch, R.F., Separation of long chain fatty acids as phenacyl esters by high pressure liquid chromatography, *Anal. Chem.*, 47, 2437, 1975.
39. Poole, C.F., Singhawangcha, S., Zlatkis, A., and Morgan, E.D., Polynuclear aromatic boronic acids as selective fluorescent reagents for HPTLC and HPLC, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 1, 96, 1978.
40. Björkqvist, B. and Toivonen, H., Separation and determination of aliphatic alcohols by high-performance liquid chromatography with U.V. detection, *J. Chromatogr.*, 153, 265, 1978.
41. Munger, D., Sternson, L.A., Repta, A.J., and Higuchi, T., High-performance liquid chromatographic analysis of dianhydrogalactitol in plasma by derivatization with sodium diethyldithiocarbamate, *J. Chromatogr.*, 143, 375, 1977.
42. Sugiura, T., Hayashi, T., Kawai, S., and Ohno, T., High speed liquid chromatographic determination of putrescine, spermidine and spermine, *J. Chromatogr.*, 110, 385, 1975.
43. Suzuki, Y. and Tani, K., High-speed liquid-chromatography of the aliphatic alcohols as their trityl ether derivatives, *Bunseki Kagaku*, 28, 610, 1979.

### Derivatizing Reagents for HPLC

Derivatizing Reagent	Structure/Formula	Notes
<i>N</i> -(9-Acridinyl) maleimide		Used for the precolumn preparation of fluorescent derivatives of thiols Reference: 1
9-Anthryldiazomethane		Used for the precolumn preparation of fluorescent derivatives of carboxylic acids; reagent reacts well with fatty acids at room temperature to give intensely fluorescent esters Reference: 2
Benzoyl chloride		Used to introduce chromophores into alcohols and amines using pyridine as a solvent; efficient means for the isolation of carbohydrates in complex mixtures Reference: 3
Benzyl bromide		Used to introduce chromophores into carboxylic acids Reference: 4
4-Bromomethyl-6,7-dimethoxycoumarin		Used for the precolumn preparation of fluorescent derivatives of carboxylic acids using acetone as solvent and with crown ether and alkali as catalysts Reference: 5
4-Bromomethyl-7-methoxycoumarin (Br-Mmc)		Used for the precolumn preparation of fluorescent derivatives of carboxylic acids, using a crown ether (18-crown-6) as a catalyst Reference: 6

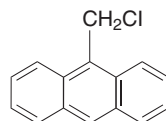


*p*-Bromophenacyl  
bromide



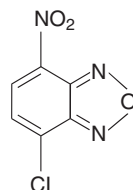
Used to introduce chromophores into carboxylic acids; crown ethers are used as phase transfer agents (for example, 18-crown-6 and dicyclohexyl-18-crown-6)  
Reference: 4

9-(Chloromethyl)  
anthracene (9-CIMA)



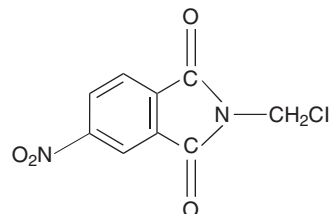
Used for the precolumn preparation of fluorescent derivatives of carboxylic acids, using cyclohexane as a solvent  
Reference: 7

4-Chloro-7-nitrobenzo-  
2-oxa-1,3-diazole  
(NBD-Cl)



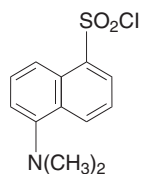
Used for the precolumn preparation of fluorescent derivatives of primary and secondary amines, phenols, and thiols (4-chloro-7-nitrobenzofuran)  
Reference: 8

*N*-Chloromethyl-4-  
nitrophthalimide



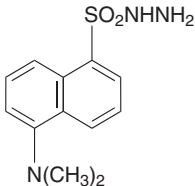
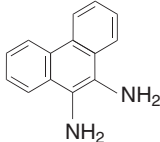
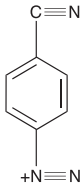
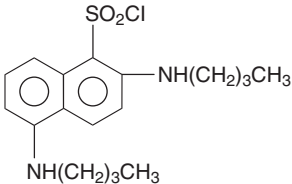
Used to introduce chromophores into carboxylic acids  
Reference: 9

Dansyl chloride  
(DnS-Cl)

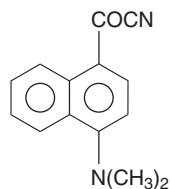


Used for the precolumn preparation of fluorescent derivatives of primary and secondary amines, phenols, amino acids, and imidazoles  
Reference: 10

### Derivatizing Reagents for HPLC (continued)

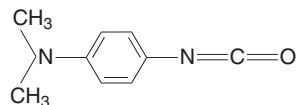
Derivatizing Reagent	Structure/Formula	Notes
Dansyl hydrazine (DnS-H)		Used for the precolumn preparation of fluorescent derivatives of aldehydes and ketones; optimal derivatization of glucose and other sugars occurs at pH 2–3 Reference: 11
9,10-Diaminophenanthrene		Used for the precolumn preparation of fluorescent derivatives of carboxylic acids Reference: 12
Diazo-4-aminobenzonitrile		Used to introduce chromophores in phenols Reference: 13
2,5-Di- <i>n</i> -butylamino-naphthalene-1-sulfonyl chloride (BnS-Cl)		Used for the precolumn preparation of fluorescent derivatives of primary and secondary amines, phenols, amino acids, and imidazoles Reference: 10

4-Dimethylamino-1-naphthoyl nitrile



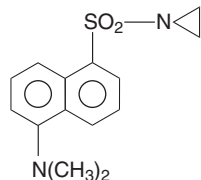
Used for the precolumn preparation of fluorescent derivatives of primary and secondary (but not tertiary) alcohols  
Reference: 14

*p*-Dimethylaminophenyl isocyanate



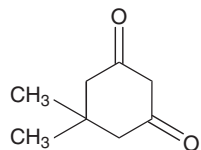
Used to introduce chromophores into alcohols; after reaction, excess reagent must be removed as it interferes with ensuing analysis  
Reference: 15

5-Dimethylamino-naphthalene 1-sulfonylaziridine (dansylaziridine)



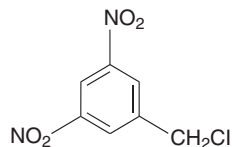
Used for the precolumn preparation of fluorescent derivatives of thiols; optimum derivatization conditions were found to be pH 8.2 with a minimum of a 2.7-fold molar reagent excess using a reaction time of 1 h at 60°C; under these conditions only free sulfhydryl groups are derivatized  
Reference: 16

5,5-Dimethyl-1,3-cyclohexanedione (dimedone)



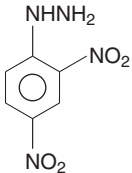
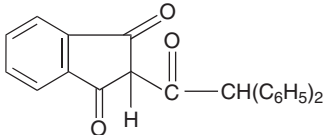
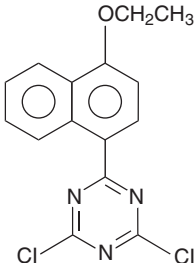
Used for the precolumn preparation of fluorescent derivatives of aldehydes, using isopropanol as a solvent in the presence of ammonium acetate  
Reference: 17

3,5-Dinitrobenzyl chloride

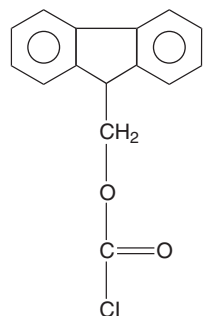


Used to introduce chromophores into amines (forming phenyl-substituted amines), alcohols, glycols, and phenols  
References: 18, 19

### Derivatizing Reagents for HPLC (continued)

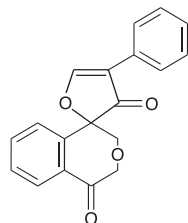
Derivatizing Reagent	Structure/Formula	Notes
2,4-Dinitrophenyl-hydrazine		Used to introduce chromophores into aldehydes and ketones in a solution of carbonyl-free methanol; detection of the more common 17-keto steroids as their 2,4-dinitrophenyl derivatives from urine and plasma; suggested potential for clinical use Reference: 20
2-Diphenylacetyl-1,3-indandione		Used for the precolumn preparation of fluorescent derivatives of aldehydes and ketones; reagent suggested to be especially useful because of its application on the microlevel, for the analysis and identification of carbonyl compounds in smog, polluted air, and biochemical and pharmaceutical mixtures; reagent does not appear to be useful for analysis of sugars; derivatives are fluorescent in the UV as solids and in solution References: 21, 22
1-Ethoxy-4-(dichloro-s-triazinyl) naphthalene or EDTN		Used for the precolumn preparation of fluorescent derivatives of primary and secondary alcohols and phenols Reference: 23

9-Fluorenylmethyl  
chloroformate  
(FMOCCl)



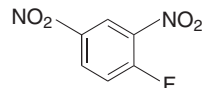
Used for the precolumn preparation of fluorescent derivatives of primary and secondary amines in acetone solvent; in the presence of sodium borate, derivation proceeds rapidly under alkaline conditions  
Reference: 24

Fluorescamine or fluram



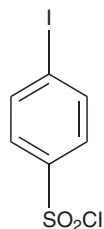
Used for the precolumn preparation of fluorescent derivatives of primary amines and amino acids by HPLC  
Reference: 10

1-Fluoro-2,4-dinitro  
benzene



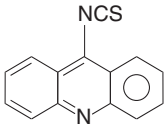
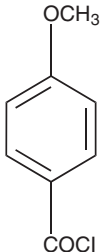
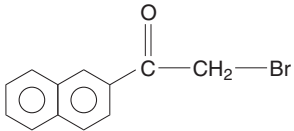
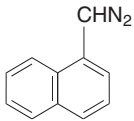
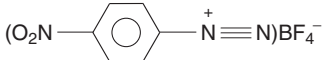
Used to introduce chromophores into amines using Sanger's procedure  
Reference: 25

*p*-Iodobenzensulfonyl  
chloride

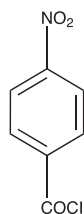


Used to introduce chromophores into alcohols and phenols; aids in separation of estrogen derivatives  
Reference: 26

### Derivatizing Reagents for HPLC (continued)

Derivatizing Reagent	Structure/Formula	Notes
9-Isothiocyanato-acridine		Used for the precolumn preparation of fluorescent derivatives of some primary and secondary amines using toluene as a solvent; only amines with $pK_a \geq 9.33$ have been successfully determined Reference: 27
<i>p</i> -Methoxybenzoyl chloride		Used to introduce chromophores into amines using the reagent in tetrahydrofuran Reference: 28
2-Naphthacyl bromide (NPB)		Used to introduce chromophores into amines in acetone as a solvent, with cesium bromide as a catalyst; it is suggested that elevated temperatures (up to 80°C) are necessary for the complete derivatization of compounds containing diisopropylamines Reference: 29
1-Naphthyldiazo-methane		Used to introduce chromophores into carboxylic acids; reagent is prepared from 1-naphthaldehyde hydrazone by oxidation with Hg(II) oxide, with diethyl ether as a solvent; acetic acid will destroy excess reagent Reference: 30
<i>p</i> -Nitrobenzenediazoniumtetrafluoroborate		Used to introduce chromophores into phenols, suggested derivation takes place in aqueous medium at pH 11.5 Reference: 31

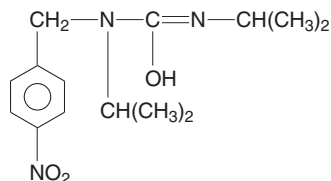
*p*-Nitrobenzoyl chloride  
(4-NBCl)



Used to introduce chromophores into alcohols and amines, using pyridine as the solvent; with silica gel as the stationary phase, relatively low-viscosity, low-polarity solvents can be used for detection of digitalis glycosides by HPLC following derivatization with *p*-nitrobenzoyl chloride

Reference: 32

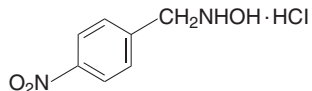
*p*-Nitrobenzyl-*N,N*-diisopropylisourea



Used to introduce chromophores into carboxylic acids, without the need for a base catalyst, and under mild conditions; picomolar concentrations are rendered detectable

Reference: 33

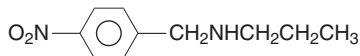
*p*-Nitrobenzyl-hydroxylamine hydrochloride



Used to introduce chromophores into ketones and aldehydes

Reference: 34

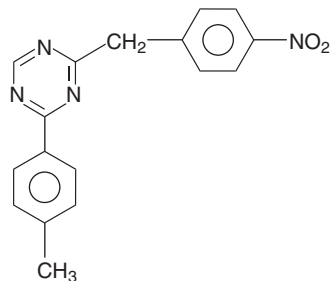
*N*-*p*-Nitrobenzyl-*N*-*n*-propylamine



Used to introduce chromophores into isocyanates; suggested for use in determining isocyanate levels in air down to 0.2 ppm in a 20-l air sample

Reference: 35

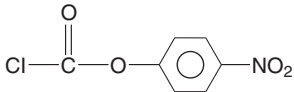
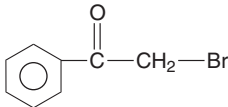
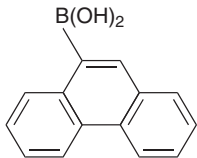
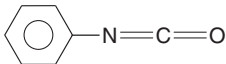
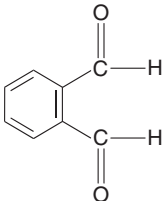
1-*p*-Nitrobenzyl-3-*p*-tolyltriazine



Used to introduce chromophores into carboxylic acids

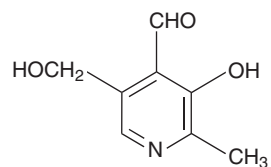
Reference: 36

### Derivatizing Reagents for HPLC (continued)

Derivatizing Reagent	Structure/Formula	Notes
<i>p</i> -Nitrophenyl chloroformate		Used to introduce chromophores into alcohols Reference: 37
Phenacyl bromide		Used to introduce chromophores into carboxylic acids; provides for the subsequent analysis of fatty acid mixtures on the microgram scale using HPLC Reference: 38
9-Phenanthreneboronic acid		Used for the precolumn preparation of fluorescent derivatives of bifunctional compounds Reference: 39
Phenyl isocyanate		Used to introduce chromophores into alcohols; thermal lability of the derivatives can cause problems; can also be used in the presence of water, but more reagent is required in this case Reference: 40
$\alpha$ -Phthalaldehyde (OPT)		Used for the precolumn preparation of fluorescent derivatives of amines and amino acids, in the presence of mercaptoethanol (or ethanethiol) and borate buffer Reference: 1



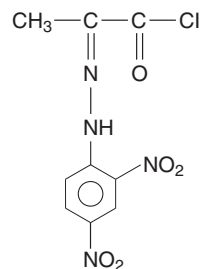
Pyridoxal



Used for the precolumn preparation of fluorescent derivatives of amino acids

Reference: 18

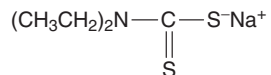
Pyruvoyl chloride (2,4-dinitrophenyl hydrazone)



Used to introduce chromophores into alcohols, amines, ketones, aldehydes, mercaptans, and phenols; aids in separation of estrogen derivatives

Reference: 26

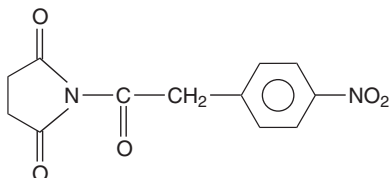
Sodium diethyldithiocarbamate (DDTC)



Used to introduce chromophores into epoxides in the presence of phosphate buffer; dithiocarbamates retain high nucleophilicity and are often water soluble

Reference: 41

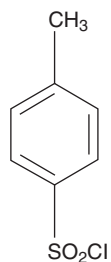
*n*-Succinimidyl-*p*-nitrophenylacetate



Used to introduce chromophores into amines; reacts under mild conditions without the need for catalysis

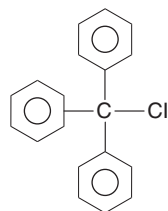
Reference: 34

*p*-Toluenesulfonyl  
chloride (TsCl)



Used to introduce chromophores into amines; aids in resolution of putrescine, spermidine, and spermine by HPLC; excess TsCl must be removed (by extraction with hexane, for example) before analysis  
Reference: 41

Trityl chloride



Used to introduce chromophores into alcohols  
Reference: 42, 43

## CHAPTER 3

# Thin-Layer Chromatography

### CONTENTS

Strength of Common TLC Solvents  
Modification of the Activity of Alumina by Addition of Water  
Stationary and Mobile Phases  
Typical Stationary and Mobile Phase Systems Used  
    in the Separation of Various Inorganic Ions  
Spray Reagents in Thin-Layer Chromatography  
Protocol for Reagent Preparation

## STRENGTH OF COMMON TLC SOLVENTS

The following table contains the common solvents used in thin-layer chromatography, with a measure of their strengths on silica gel and alumina. The solvent strength parameter,  $\epsilon^\circ$ , is defined as the relative energy of adsorption per unit area of standard adsorbent.<sup>1-3</sup> It is defined as zero on alumina when pentane is used as the solvent. This series is what was called the eluotropic series in the older literature. For convenience, the solvent viscosity is also provided. Note that the viscosity is tabulated in cP for the convenience of most users. This is equivalent to mPa·sec in the SI convention. Additional data on these solvents may be found in the tables on high-performance liquid chromatography.

## REFERENCES

1. Snyder, L.R., *Principles of Adsorption Chromatography*, Marcel Dekker, New York, 1968.
2. Willard, H.H., Merritt, L.L., Dean, J.A., and Settle, F.A., *Instrumental Methods of Analysis*, 7th ed., Van Nostrand, New York, 1988.
3. Hamilton, R. and Hamilton, S., *Thin Layer Chromatography*, John Wiley & Sons, Chichester, 1987 (on behalf of "Analytical Chemistry by Open Learning," London).

### Strength of Common TLC Solvents

Solvent <sup>a</sup>	$\epsilon^\circ(\text{Al}_2\text{O}_3)$	Viscosity, cP, 20°	$\epsilon^\circ(\text{SiO}_2)$
Fluoroalkanes	~-0.25	—	
<i>n</i> -Hexane	0.00	0.23	0.00
<i>n</i> -Pentane	0.001	0.23	0.00
2,2,4-Trimethylpentane (isooctane)	0.01	0.54	
<i>n</i> -Heptane	0.01	0.41	
<i>n</i> -Decane	0.04	0.92	
Cyclohexane	0.04	1.00	-0.05
Cyclopentane	0.05	0.47	
Carbon disulfide	0.15	0.37	0.14
Tetrachloromethane (carbon tetrachloride)	0.18	0.97	
1-Chloropentane ( <i>n</i> -pentylchloride)	0.26	0.43	
Diisopropyl ether	0.28	0.37	
2-Chloropropane (isopropyl chloride)	0.29	0.33	
Methylbenzene (toluene)	0.29	0.59	
1-Chloropropane ( <i>n</i> -propyl chloride)	0.30	0.35	
Chlorobenzene	0.30	0.80	
Benzene	0.32	0.65	0.25
Bromoethane (ethyl bromide)	0.37	0.41	
Diethyl ether (ether)	0.38	0.23	0.38
Trichloromethane (chloroform)	0.40	0.57	
Dichloromethane (methylene chloride)	0.42	0.44	
Tetrahydrofuran (THF)	0.45	0.55	
1,2-Dichloroethane	0.49	0.79	
Butanone (methyl ethyl ketone)	0.51	0.43	
Propanone (acetone)	0.56	0.32	0.47
1,4-Dioxane	0.56	1.54	0.49
Ethyl ethanoate (ethyl acetate)	0.58	0.45	0.38
Methyl ethanoate (methyl acetate)	0.60	0.37	
1-Pentanol ( <i>n</i> -pentanol)	0.61	4.1	
Dimethyl sulfoxide (DMSO)	0.62	2.24	
Aminobenzene (aniline)	0.62	4.4	
Nitromethane	0.64	0.67	
Cyanomethane (acetonitrile)	0.65	0.37	0.50
Pyridine	0.71	0.94	
2-Propanol (isopropanol)	0.82	2.3	
Ethanol	0.88	1.20	
Methanol	0.95	0.60	
Ethylene glycol	1.11	19.9	
Ethanoic acid (acetic acid)	Large	1.26	
Water	Large	1.00	

<sup>a</sup> The common, or generic, name of the solvent is provided parenthetically.

## MODIFICATION OF THE ACTIVITY OF ALUMINA BY ADDITION OF WATER

The following table describes five different activity grades of commercial alumina used in chromatography.<sup>1-3</sup> The activity grades are defined by the degree of adsorption of azobenzene (called azobenzene number) on the types of hydrated alumina. Those types are prepared by heating commercial alumina to redness, giving grade I, and then adding controlled amounts of water and allowing equilibration in a closed vessel. The azobenzene number decreases with the amount of water added. The  $R_f$  value is the ratio of distance traveled by the solute spot to that traveled by the solvent.

## REFERENCES

1. Randerath, K., *Thin Layer Chromatography*, Verlag Chemie-Academic Press, New York, 1968.
2. Gordon, A.J. and Ford, R.A., *The Chemist's Companion: A Handbook of Practical Data, Techniques, and References*, John Wiley & Sons, New York, 1972.
3. Brockmann, H. and Schodder, H., Aluminum oxide with buffered adsorptive properties for purposes of chromatographic adsorption, *Berl. Dtsch. Chem. Ges.*, 74B, 73, 1941.

Modification of the Activity of Alumina by Addition of Water

Water Added (w/w%)	Activity Grade	Azobenzene Number (Maximum Adsorption of Azobenzene, $10^{-5}$ mol/g)	$R_f$ ( <i>p</i> -Amino- Azobenzene)
0	I	26	0.00
3	II	21	0.13
6	III	18	0.25
10	IV	13	0.45
15	V	0	0.55

## STATIONARY AND MOBILE PHASES

The following table provides a comprehensive guide to the selection of thin-layer chromatography media and solvents for a given chemical family. Mixed mobile phases are denoted with a slash, /, between components and where available the proportions are given. Among the references are several excellent texts,<sup>1-3,60</sup> review articles,<sup>4-24</sup> and original research papers and reports.<sup>25-59,61-98</sup> A table of abbreviations follows this section.

## REFERENCES

1. Krebs, K.G., Heusser, D., and Wimmer, H., in *Thin Layer Chromatography, A Laboratory Handbook*, Stahl, E., Ed., Springer-Verlag, New York, 1969.
2. Bobbitt, J.B., *Thin Layer Chromatography*, Reinhold, New York, 1963.
3. Touchstone, J.C., *Techniques and Application of Thin Layer Chromatography*, John Wiley, New York, 1985.
4. Pataki, G., Paper, thin-layer, and electrochromatography of amino acids in biological material, *Z. Klin. Chem.*, 2, 129, 1964; *Chem. Abs.*, 64, 5425c, 1966.
5. Padley, F.B., Thin-Layer Chromatography of Lipids, paper presented at the Thin-Layer Chromatography Proceedings Symposium, Rome 1963, 87 (published in 1964).
6. Honjo, M., Thin-layer chromatography of nucleic acid derivatives, *Kagaku No Ryoiki Zokan*, 64, 1, 1964.
7. Kazumo, T., Thin-layer chromatography of bile acids, *Kagaku No Ryoiki Zokan*, 64, 19, 1964.
8. Nakazawa, Y., Thin-layer chromatography of compound lipids, *Kagaku No Ryoiki Zokan*, 64, 31, 1964.
9. Nishikaze, O., Separation and quantitative analysis of adrenocortical hormone and its metabolite (C<sub>21</sub>) by thin-layer chromatography, *Kagaku No Ryoiki Zokan*, 64, 37, 1964.
10. Shikita, M., Kakizaki, H., and Tamaoki, B., Thin-layer chromatography of radioactive substances, *Kagaku No Ryoiki Zokan*, 64, 45, 1964.
11. Mo, I. and Hashimoto, Y., Method of thin-layer zone electrophoresis, *Kagaku No Ryoiki Zokan*, 64, 61, 1964.
12. Kinoshita, S., Thin-layer chromatography of sugar esters, *Kagaku No Ryoiki Zokan*, 64, 79, 1964.
13. Okada, M., Thin-layer chromatography of cardiotonic glycosides, *Kagaku No Ryoiki Zokan*, 64, 103, 1964.
14. Omoto, T., Thin-layer chromatography of toad toxin, *Kagaku No Ryoiki Zokan*, 64, 115, 1964.
15. Furuya, C. and Itokawa, H., Thin-layer chromatography of triterpenoids, *Kagaku No Ryoiki Zokan*, 64, 123, 1964.
16. Zenda, H., Thin-layer chromatography of aconitine-type alkaloids, *Kagaku No Ryoiki Zokan*, 64, 133, 1964.
17. Hara, S. and Tanaka, H., Thin-layer chromatography of mixed pharmaceutical preparations, *Kagaku No Ryoiki Zokan*, 64, 141, 1964.
18. Katsui, G., Thin-layer chromatography of vitamins, *Kagaku No Ryoiki Zokan*, 64, 157, 1964.
19. Fujii, S. and Kamikura, M., Thin-layer chromatography of pigments, *Kagaku No Ryoiki Zokan*, 64, 173, 1964.
20. Hosogai, Y., Thin-layer chromatography of organic chlorine compounds, *Kagaku No Ryoiki Zokan*, 64, 185, 1964.
21. Takeuchi, T., Thin-layer chromatography of metal complex salts, *Kagaku No Ryoiki Zokan*, 64, 197, 1964.
22. Yamakawa, H. and Tanigawa, K., Thin-layer chromatography of organic metal compounds, *Kagaku No Ryoiki Zokan*, 64, 209, 1964.
23. Takitani, S. and Kawanabe, K., Thin-layer chromatography of inorganic ions (anions), *Kagaku No Ryoiki Zokan*, 64, 221, 1964.
24. Ibayashi, H., Thin-layer chromatography of steroid hormones and its clinical application, *Kagaku No Ryoiki Zokan*, 64, 227, 1964.

25. Chilingarov, A.O. and Sobchinskaya, N.M., Quantitative ultramicroanalysis of monoamine dansyl derivatives in biological material, *Lab. Delo*, 333, 1980; *Chem. Abs.*, 93, 109910t, 1980.
26. Heacock, R.A., Nerenberg, C., and Payza, A.N., The chemistry of the "aminochromes." Part I. The preparation and paper chromatography of pure adrenochrome, *Can. J. Chem.*, 36, 853, 1958.
27. Heacock, R.A. and Powell, W.S., Adrenochrome and related compounds, *Prog. Med. Chem.*, 9, 275, 1972.
28. Heacock, R.A. and Scott, B.D., The chemistry of the "aminochromes." Part IV. Some new aminochromes and their derivatives, *Can. J. Chem.*, 38, 516, 1960.
29. Heacock, R.A., The chemistry of adrenochrome and related compounds, *Chem. Rev.*, 59, 181, 1959.
30. Suryaraman, M.G. and Cave, W.T., Detection of some aliphatic saturated long chain hydrocarbon derivatives by thin-layer chromatography, *Anal. Chim. Acta*, 30, 96, 1964; *Chem. Abs.*, 60, 7463e, 1964.
31. Knappe, E., Peteri, D., and Rohdewald, I., Thin-layer chromatographic identification of technically important polyhydric alcohols, *Z. Anal. Chem.*, 199, 270, 1964; *Chem. Abs.*, 60, 7464f, 1964.
32. Horak, V. and Klein, R.F.X., Microscale group test for carbonyl compounds, *J. Chem. Educ.*, 62, 806, 1985.
33. Jaminet, F., Paper microchromatography in phytochemical analysis: application to Congolian Strychnos, *J. Pharm. Belg.*, 8, 339 and 449, 1953; *Chem. Abs.*, 48, 8482c, 1954.
34. Neu, R., A new color method for determining alkaloids and organic bases with sodium tetraphenylborate, *J. Chromatogr.*, 11, 364, 1963; *Chem. Abs.*, 59, 12181d, 1963.
35. Marini-Bettolo, B.G. and Caggiano, E., Paper chromatography and electrophoresis of tertiary bases, a symposium organized by the Chromatography Group of the Czechoslovak Chemical Society at Liblice Czech., June 23, 1961, p. 91; *Chem. Abs.*, 60, 838d, 1964.
36. Knappe, E. and Rohdewald, I., Impregnation of chromatographic thin layers with polyesters. III. Thin-layer chromatographic identification of acetoacetic acid amides, *Z. Anal. Chem.*, 208, 195, 1965; *Chem. Abs.*, 62, 12424f, 1965.
37. Lane, E.S., Thin-layer chromatography of long-chain tertiary amines and related compounds, *J. Chromatogr.*, 18, 426, 1965; *Chem. Abs.*, 63, 7630f, 1965.
38. Ashworth, M.R.F. and Bohnstedt, G., Reagent for the detection and determination of N-active hydrogen, *Talanta*, 13, 1631, 1966; *Chem. Abs.*, 66, 25889x, 1967.
39. Heacock, R.A., The aminochromes, in *Advances in Heterocyclic Chemistry*, Katritsky, A.R., Ed., Academic Press, New York, 1965, p. 205; *Chem. Abs.*, 65, 5432d, 1966.
40. Knappe, E., Peteri, D., and Rohdewald, I., Impregnation of chromatographic thin layers with polyesters for the separation and identification of substituted 2-hydroxybenzophenones and other ultraviolet absorbers, *Z. Anal. Chem.*, 197, 364, 1963; *Chem. Abs.*, 60, 762g, 1964.
41. Hara, S. and Takeuchi, M., Systematic analysis of bile acids and their derivatives by thin layer chromatography, *J. Chromatogr.*, 11, 565, 1963; *Chem. Abs.*, 60, 838f, 1964.
42. Hauck, A., Detection of caffeine by paper chromatography, *Deut. Z. Gerichtl. Med.*, 54, 98, 1963; *Chem. Abs.*, 60, 838b, 1964.
43. Knappe, E. and Rohdewald, I., Thin-layer chromatography of dicarboxylic acids. IV. Combination of thin-layer chromatographic systems for the identification of individual components in dicarboxylic acid mixtures, *Z. Anal. Chem.*, 210, 183, 1965; *Chem. Abs.*, 63, 3600f, 1965.
44. Passera, C., Pedrotti, A., and Ferrari, G., Thin-layer chromatography of carboxylic acids and ketoacids of biological interest, *J. Chromatogr.*, 14, 289, 1964; *Chem. Abs.*, 60, 16191f, 1964.
45. Knappe, E. and Peteri, D., Thin-layer chromatography of dicarboxylic acids. I. Separations in the homologous series oxalic to sebacic acids, *Z. Anal. Chem.*, 188, 184, 1962; *Chem. Abs.*, 57, 11836a, 1962.
46. Peteri, D., Thin-layer chromatography of dicarboxylic acids. II. Separation of carbocyclic dicarboxylic acids, *Z. Anal. Chem.*, 158, 352, 1962; *Chem. Abs.*, 57, 11836b, 1962.
47. Dutta, S.P. and Baruta, A.K., Separation of cis- and trans-isomers of  $\alpha,\beta$ -unsaturated acids by thin-layer chromatography, *J. Chromatogr.*, 29, 263, 1967; *Chem. Abs.*, 67, 96616n, 1967.
48. Dalmaz, Y. and Peyrin, L., Rapid procedure for chromatographic isolation of DOPA, DOPAC, epinephrine, norepinephrine and dopamine from a single urinary sample at endogenous levels, *J. Chromatogr.*, 145, 11, 1978; *Chem. Abs.*, 88, 59809c, 1978.
49. Baumgartner, H., Ridl, W., Klein, G., and Preindl, S., Improved radioenzymic assay for the determination of catecholamines in plasma, *Clin. Chim. Acta*, 132, 111, 1983; *Chem. Abs.*, 99, 99459k, 1983.



50. Hansson, C., Agrup G., Rorsman, H., Rosengren, A.M., and Rosengren, E., Chromatographic separation of catecholic amino acids and catecholamines on immobilized phenylboronic acid, *J. Chromatogr.*, 161, 352, 1978; *Chem. Abs.*, 90, 50771d, 1979.
51. Endo, Y. and Ogura, Y., Separation of catecholamines on the phosphocellulose column, *Jap. J. Pharmacol.*, 23, 491, 1973; *Chem. Abs.*, 80, 12002s, 1974.
52. Wada, H., Yamatodani, A., and Seki, T., Systematic determination of amino acids, amines and some nucleotides using dansylchloride, *Kagaku No Ryoiki Zokan*, 114, 1, 1976; *Chem. Abs.*, 87, 1904f, 1977.
53. Head, R.J., Irvine, R.J., and Kennedy, J.A., The use of sodium borate impregnated silica gel plates for the separation of 3-O-methyl catecholamines from their corresponding catecholamines, *J. Chromatogr. Sci.*, 14, 578, 1976; *Chem. Abs.*, 86, 39601x, 1977.
54. Adamec, O., Matis, J., and Galvanek, M., Fractionation and quantitative determination of urinary 17-hydroxycorticosteroids by thin layer chromatography on silica gel, *Steroids*, 1, 495, 1963.
55. Adamec, O., Matis, J., and Galvanek, M., Chromatographic separation of corticoids on a thin layer of silica gel, *Lancet*, I, 81, 1962; *Chem. Abs.*, 56, 9034d, 1962.
56. Knappe, E. and Rohdewald, I., Thin-layer chromatography of dicarboxylic acids. V. Separation and identification of hydroxy dicarboxylic acids, of di- and tricarboxylic acids of the citrate cycle, and some other dicarboxylic acids of plant origin, *Z. Anal. Chem.*, 211, 49, 1965; *Chem. Abs.*, 63, 7333c, 1965.
57. Snegotskii, V.I. and Snegotskaya, V.A., Thin-layer chromatography of sulfur compounds, *Zavod. Lab.*, 35, 429, 1969; *Chem. Abs.*, 71, 23436b, 1969.
58. Borecky, J., Gasparic, J., and Vecera, M., Identification of organic compounds. XXV. Identification and separation of aliphatic C<sub>1</sub>-C<sub>18</sub> alcohols by paper chromatography, *Chem. Listy*, 52, 1283, 1958; *Chem. Abs.*, 53, 8039h, 1958.
59. Hörhammer, L., Wagner, H., and Hein, H., Thin-layer chromatography of flavonoids on silica gel, *J. Chromatogr.*, 13, 235, 1964; *Chem. Abs.*, 60, 13856c, 1964.
60. Mikes, O., Ed., *Laboratory Handbook of Chromatographic Methods*, D. Van Nostrand Co., Ltd., London, 1966.
61. Wright, J., Detection of humectants in tobacco by thin layer chromatography, *Chem. Ind. (London)*, 1963, 1125.
62. Korte, F. and Vogel, J., Thin-layer chromatography of lactones, lactams and thiolactones, *J. Chromatogr.*, 9, 381, 1962; *Chem. Abs.*, 58, 9609c, 1963.
63. Heacock, R.A. and Mahon, M.E., Paper chromatography of some indole derivatives on acetylated paper, *J. Chromatogr.*, 6, 91, 1961.
64. Hackman, R.H. and Goldberg, M., Microchemical detection of melanins, *Anal. Biochem.*, 41, 279, 1971; *Chem. Abs.*, 74, 136114a, 1971.
65. Preussmann, R., Neurath, G., Wulf-Lorentzen, G., Daiber, D., and Hengy, H., Color formation and thin-layer chromatography for N-nitrosocompounds, *Z. Anal. Chem.*, 202, 187, 1964.
66. Preussmann, R., Daiber, D., and Hengy, H., Sensitive color reaction for nitrosamines on thin-layer chromatography, *Nature*, 201, 502, 1964; *Chem. Abs.*, 60, 12663e, 1964.
67. Hranisavljevic-Jakovljevic, M., Pejtkovic-Tadic, I., and Stojiljkovic, A., Thin-layer chromatography of isomeric oximes, *J. Chromatogr.*, 12, 70, 1963; *Chem. Abs.*, 60, 7d, 1964.
68. Abraham, M.H., Davies, A.G., Llewellyn, D.R., and Thain, E.M., The chromatographic analysis of organic peroxides, *Anal. Chim. Acta*, 17, 499, 1957; *Chem. Abs.*, 53, 120b, 1959.
69. Seeboth, H., Thin-layer chromatography analysis of phenols, *Monatsber. Deut. Akad. Wiss. Berl.*, 5, 693, 1963; *Chem. Abs.*, 61, 2489c, 1964.
70. Knappe, E. and Rohdewald, I., Thin-layer chromatographic identification of simple phenols using the coupling products with Fast Red Salt AL, *Z. Anal. Chem.*, 200, 9, 1964; *Chem. Abs.*, 60, 9913g, 1964.
71. Donner, R. and Lohs, K., Cobalt chloride in the detection of organic phosphate ester by paper and especially thin-layer chromatography, *J. Chromatogr.*, 17, 349, 1965; *Chem. Abs.*, 62, 13842d, 1965.
72. Engel, J.F. and Barney, J.E., Chromatographic separation of hydrogenation products of dibenz[a,h]anthracene, *J. Chromatogr.*, 29, 232, 1967; *Chem. Abs.*, 57, 96617p, 1967.
73. Kucharczyk, N., Fohl, J., and Vymetal, J., Thin-layer chromatography of aromatic hydrocarbons and some heterocyclic compounds, *J. Chromatogr.*, 11, 55, 1963; *Chem. Abs.*, 59, 9295g, 1963.
74. Perifoy, P.V., Slaymaker, S.C., and Nager, M., Tetracyanoethylene as a color-developing reagent for aromatic hydrocarbons, *Anal. Chem.*, 31, 1740, 1959; *Chem. Abs.*, 54, 5343e, 1960.

75. Kodicek, E. and Reddi, K.K., Chromatography of nicotinic acid derivatives, *Nature*, 168, 475, 1951; *Chem. Abs.*, 46, 3601g, 1952.
76. Heacock, R.A. and Mahon, M.E., The color reactions of the hydroxyskatoles, *J. Chromatogr.*, 17, 338, 1965; *Chem. Abs.*, 62, 13824g, 1965.
77. Martin, H.P., Reversed phase paper chromatography and detection of steroids of the cholesterol class, *Biochim. Biophys. Acta*, 25, 408, 1957.
78. Lisboa, B.P., Application of thin-layer chromatography to the steroids of the androstane series, *J. Chromatogr.*, 13, 391, 1964; *Chem. Abs.*, 60, 13890b, 1964.
79. Lisboa, B.P., Separation and characterization of  $\Delta^5$ -3-hydroxy- $C_{19}$ -steroids by thin-layer chromatography, *J. Chromatogr.*, 19, 333, 1965; *Chem. Abs.*, 63, 16403h, 1965.
80. Lisboa, B.P., Thin-layer chromatography of  $\Delta^4$ -3-oxosteroids of the androstane series, *J. Chromatogr.*, 19, 81, 1965; *Chem. Abs.*, 63, 13619e, 1965.
81. Lisboa, B.P., Thin-layer chromatography of steroids, *J. Pharm. Belg.*, 20, 435, 1965; *Chem. Abs.*, 65, 570c, 1966.
82. Partridge, S.M., Aniline hydrogen phthalate as a spraying reagent for chromatography of sugars, *Nature*, 164, 443, 1949.
83. Grossert, J.S. and Langler, R.F., A new spray reagent for organosulfur compounds, *J. Chromatogr.*, 97, 83, 1974; *Chem. Abs.*, 82, 25473n, 1976.
84. Petranek, J. and Vecera, M., Identification of organic compounds. XXIV. Separation and identification of sulfides by paper chromatography, *Chem. Listy*, 52, 1279, 1958; *Chem. Abs.*, 53, 8039d, 1958.
85. Bican-Fister, T. and Kajganovic, V., Quantitative analysis of sulfonamide mixtures by thin-layer chromatography, *J. Chromatogr.*, 16, 503, 1964; *Chem. Abs.*, 62, 8943d, 1965.
86. Bican-Fister, T. and Kajganovic, V., Separation and identification of sulfonamides by thin-layer chromatography, *J. Chromatogr.*, 11, 492, 1963; *Chem. Abs.*, 60, 372f, 1964.
87. Reisch, J., Bornfleth, H., and Rheinbay, J., Thin-layer chromatography of some useful sulfonamides, *Pharm. Ztg. Ver. Apotheker-Ztg.*, 107, 920, 1962; *Chem. Abs.*, 60, 372e, 1964.
88. Prinzler, H.W., Tauchmann, H., and Tzcharnke, C., Thin-layer chromatographic separation of organic sulfoxides and dinitrothioethers: some observations on reproducibility and structural influence. II. Separation of sulfoxide mixtures by one- and two-dimensional thin layer chromatography, *J. Chromatogr.*, 29, 151, 1967; *Chem. Abs.*, 67, 96615m, 1967.
89. Wolski, T., Color reactions for the detection of sulfoxides, *Chem. Anal. (Warsaw)*, 14, 1319, 1969; *Chem. Abs.*, 72, 106867q, 1970.
90. Bergstrom, G. and Lagercrantz, C., Diphenylpicrylhydrazyl as a reagent for terpenes and other substances in thin-layer chromatography, *Acta Chem. Scand.*, 18, 560, 1964; *Chem. Abs.*, 61, 2491h, 1964.
91. Dietz, W. and Soehring, K., Identification of thiobarbituric acids in urine by paper chromatography, *Arch. Pharm.*, 290, 80, 1957; *Chem. Abs.*, 52, 4736d, 1958.
92. Curtis, R.F. and Phillips, C.T., Thin-layer chromatography of thiophene derivatives, *J. Chromatogr.*, 9, 366, 1962; *Chem. Abs.*, 58, 10705c, 1963.
93. Salame, M., Detection and separation of the most important organophosphorus pesticides by thin-layer chromatography, *J. Chromatogr.*, 16, 476, 1964; *Chem. Abs.*, 62, 11090b, 1965.
94. Knappe, E. and Rohdewald, I., Thin-layer chromatography of substituted ureas and simple urethanes, *Z. Anal. Chem.*, 217, 110, 1966; *Chem. Abs.*, 64, 16601g, 1966.
95. Fishbein, L. and Fawkes, J., Detection and thin-layer chromatography of sulfur compounds. I. Sulfoxides, sulfones and sulfides, *J. Chromatogr.*, 22, 323, 1966; *Chem. Abs.*, 65, 6281e, 1966.
96. Prinzler, H.W., Pape, D., Tauchmann, H., Teppke, M., and Tzcharnke, C., Thin-layer chromatography of organic sulfur compounds, *Ropa Uhlje*, 8, 13, 1966; *Chem. Abs.*, 65, 9710h, 1966.
97. Karaulova, E.N., Bobruiskaya, T.S., and Gal'pern, G.D., Thin-layer chromatography of sulfoxides, *Zh. Analit. Khim.*, 21, 893, 1966; *Chem. Abs.*, 65, 16046f, 1966.
98. Knappe, E. and Yekundi, K.G., Impregnation of chromatographic thin layers with polyesters. II. Separation and identification of lower and middle fatty acids via the hydroxamic acid, *Z. Anal. Chem.*, 203, 87, 1964; *Chem. Abs.*, 61, 5915e, 1964.

**Abbreviations/Solvent Table**

<b>Abbreviation</b>	<b>Solvent Name</b>	<b>Abbreviation</b>	<b>Solvent Name</b>
Ac	Acetone	Et <sub>2</sub> O	Diethyl ether
Ace	Acetate	Foram	Amylformate
AcOH	Acetic acid	HCl	Hydrochloric acid
<i>n</i> -AmOH	<i>n</i> -Amyl alcohol	H <sub>3</sub> BO <sub>3</sub>	Boric acid
<i>t</i> -AmOH	<i>t</i> -Amyl alcohol	Hex	Hexane
AmSO <sub>4</sub>	Ammonium sulfate	HForm	Formic acid
<i>i</i> -BuAc	Isobutyl acetate	MeCl	Methylene chloride
BuFor	<i>n</i> -Butyl formate	MeCN	Acetonitrile
<i>i</i> -BuOH	Isobutanol	MEK	Methylethylketone
<i>n</i> -BuOH	<i>n</i> -Butanol	MeOH	Methanol
<i>i</i> -Bu <sub>2</sub> O	Diisobutylether	NaAc	Sodium acetate
CCl <sub>4</sub>	Carbon tetrachloride	NH <sub>3</sub>	Ammonia
C <sub>2</sub> HCl <sub>3</sub>	Trichloroethene	Petet	Petroleum ether
CHCl <sub>3</sub>	Chloroform	Ph	Phosphate
(CH <sub>2</sub> ) <sub>6</sub>	Cyclohexane	PhOH	Phenol
C <sub>6</sub> H <sub>6</sub>	Benzene	PrAc	Propylacetate
<i>n</i> -C <sub>6</sub> H <sub>14</sub>	<i>n</i> -Hexane	PrFor	Propylformate
<i>n</i> -C <sub>7</sub> H <sub>16</sub>	<i>n</i> -Heptane	Progl	Propylene glycol
<i>i</i> -C <sub>8</sub> H <sub>18</sub>	Isooctane	<i>i</i> -PrOH	Isopropanol
(ClCH <sub>2</sub> ) <sub>2</sub>	Dichloroethane	<i>n</i> -PrOH	<i>n</i> -Propanol
DEAE	Diethyl aminoethyl	<i>i</i> -Pr <sub>2</sub> NH	Diisopropylamine
Diox	Dioxane	<i>i</i> -Pr <sub>2</sub> O	Diisopropylether
DMF	Dimethyl formamide	Py	Pyridine
EtFor	Ethyl formate	THF	Tetrahydrofuran
EtOAc	Ethyl acetate	Tol	Toluene
EtOH	Ethanol	w	Water
Et <sub>2</sub> NH	Diethylamine	<i>m</i> -X	<i>m</i> -Xylene

# Stationary and Mobile Phases

Family	Stationary Phase	Mobile Phase	Reference
Adrenaline and derivatives	Alumina (two-dimensional)	C <sub>6</sub> H <sub>6</sub> /EtOAc (60:40) CHCl <sub>3</sub> /EtOH/Tol (90:6.5:3.1)	25
Adrenochromes	Cellulose Whatman 1 (descending)	AcOH(2%)/w AcOH(2%)/w	26, 27 26–29
Alcohols	Silica gel G	EtOAc/Hex	30
Alcohols, polyhydric	Alumina or Kieselguhr (impregnated with polyamide) or silica gel	CHCl <sub>3</sub> /Tol/HForm or <i>n</i> -BuOH/NH <sub>3</sub> or CHCl <sub>3</sub>	31
Aldehydes	Silica gel G	EtOAc/Hex	30
Aldehydes, 2,4-dinitro-phenylhydrazones	Alumina Alumina IB Silica gel Silica gel IB	C <sub>6</sub> H <sub>6</sub> or CHCl <sub>3</sub> or Et <sub>2</sub> O or C <sub>6</sub> H <sub>6</sub> /Hex MeCl or Tol/THF (4:1) Hex/EtOAc (4:1 or 3:2) MeCl or Tol/THF (4:1)	3 32 3 32
Alkaloids	Alumina Alumina Cellulose (impregnated with formamide) Paper (S&S 2043b) Paper electrophoresis Silica gel	<i>i</i> -BuOH/AcOH or <i>i</i> -BuOH/NH <sub>3</sub> or <i>i</i> -PrOH/AcOH CHCl <sub>3</sub> or EtOH or (CH <sub>2</sub> ) <sub>6</sub> /CHCl <sub>3</sub> (3:7) C <sub>6</sub> H <sub>6</sub> / <i>n</i> -C <sub>7</sub> H <sub>16</sub> /CHCl <sub>3</sub> /Et <sub>2</sub> NH (6:5:1:0.02) <i>n</i> -BuOH/HCl(25%)/w (100:26:39) <i>i</i> -BuOH/AcOH or <i>i</i> -BuOH/NH <sub>3</sub> or <i>i</i> -PrOH/HOAc C <sub>6</sub> H <sub>6</sub> /EtOH (9:1) or CHCl <sub>3</sub> /Ac/Et <sub>2</sub> NH (5:4:1)	33 3 3 34 35 3
Amides	Kieselguhr (adipic acid impregnated) Silica gel	<i>i</i> -Pr <sub>2</sub> O/Petet/CCl <sub>4</sub> /HForm/w <i>i</i> -Pr <sub>2</sub> O/Petet/CCl <sub>4</sub> /HForm/w	36 36
Amines	Alumina Alumina G Kieselguhr G Silica gel Silica gel (aromatic only)	Ac/ <i>n</i> -C <sub>7</sub> H <sub>16</sub> (1:1) <i>i</i> -BuAc or <i>i</i> -BuAc/AcOH Ac/w (99:1) EtOH (95%)/NH <sub>3</sub> (25%) (4:1)	3 37 3 3
Amino acids	Alumina Cellulose Cellulose (two-dimensional) Silica gel	<i>n</i> -BuOH/AcOH/w (3:1:1) or Py/w <i>n</i> -BuOH/AcOH/w (4:1:1) <i>n</i> -BuOH/Ac/NH <sub>3</sub> /w (10:10:5:2) followed by <i>i</i> -PrOH/HForm/w (20:1:5) <i>n</i> -BuOH/AcOH/w (3 or 4:1:1) or PhOH/w (3:1) or <i>n</i> -PrOH/NH <sub>3</sub> (34%) (2:1)	3 3 3 3
Aminochromes	Whatman 1 (acid washed)	w or AcOH/w or MeOH/w or EtOH/w or <i>n</i> -BuOH/AcOH/w or <i>i</i> -PrOH/w	26, 39
Barbiturates	Silica gel	CHCl <sub>3</sub> / <i>n</i> -BuOH/NH <sub>3</sub> (25%) (14:8:1)	3
Benzophenones, hydroxy	Alumina or cellulose or Kieselguhr (impregnated with adipic acid triethylene glycol polyester) or silica gel	HForm/m-X	40
Bile acids	Silica gel	C <sub>6</sub> H <sub>6</sub> /Et <sub>2</sub> O (4:1) or Et <sub>2</sub> O/AcOH (99.6:0.4) or CHCl <sub>3</sub> /MeOH (9:1)	41
Caffeine	Chromatography paper	<i>n</i> -BuOH/NH <sub>3</sub> or <i>n</i> -BuOH/HForm	42
Carboxylic acids	Keiselguhr/polyethylene glycol Polyamide powder Silica gel G Silica gel (CaSO <sub>4</sub> impregnated) Silica gel/polyethylene glycol M-1000	<i>i</i> -Bu <sub>2</sub> O/HForm/w (90:7:3) <i>i</i> -Pr <sub>2</sub> O/Petet/CCl <sub>4</sub> /HForm/w (50:20:20:8:1) or MeCN/EtOAc/HForm or BuForm/EtOAc/HForm EtOH/NH <sub>3</sub> /THF <i>n</i> -PrOH/NH <sub>3</sub> or EtOH/CHCl <sub>3</sub> /NH <sub>3</sub> <i>i</i> -Pr <sub>2</sub> O/HForm/w (90:7:3)	43 43 30 44 43, 45, 46

# Stationary and Mobile Phases (continued)

Family	Stationary Phase	Mobile Phase	Reference
Carboxylic acids, unsaturated	Silica gel	CHCl <sub>3</sub> /MeOH	47
Catecholamines	Alumina	HCl (0.025 <i>N</i> )	48
	Boric acid gel (neutral pH)	Dilute acids	48
	Kieselguhr	Ph buffer (pH = 6.2)/EDTA	49
	Phenylboronate		50
	Phosphocellulose		51
Catecholamines, dansyl derivatives	Alumina (two-dimensional)	C <sub>6</sub> H <sub>6</sub> /EtOAc (60:40) or CHCl <sub>3</sub> /EtOH/Tol (90:6.5:3.5)	25
	Amberlite IRC50		52
Catecholamines, <i>o</i> -methyl derivatives	Silica gel (sodium borate impregnated)		53
Corticosteroids	Silica gel	EtOH(5%)/MeCl or EtOH/CHCl <sub>3</sub>	54, 55
Coumarins	Polyamide	MeOH/w (4:1 or 3:2)	3
	Silica gel G	Petet/EtOAc (2:1)	3
	Silica gel G (impregnated with NaAc)	Tol/EtFor/HForm (5:4:1)	3
	Silicic acid (starch bound)	EtOAc/Skellysolve B	3
Dicarboxylic acids	Kieselguhr/polyethylene glycol	<i>i</i> -Pr <sub>2</sub> O/HForm/w (90:7:3)	43
	Polyamide powder	<i>i</i> -Pr <sub>2</sub> O/Petet/CCl <sub>4</sub> /HForm/w (50:20:20:8:1) or MeCN/EtOAc/HForm (9:1:1) or BuFor/EtOAc/HForm (9:1:1)	43
	Polyamide	MeCN/PrFor/PrAc/HForm (45:45:10:10) or <i>i</i> -Pr <sub>2</sub> O/Petet/CCl <sub>4</sub> /HForm/w (50:20:20:8:1) or <i>n</i> -AmOH/CCl <sub>4</sub> /HFor (3:2:1)	56
	Woelm DC powder		
	Silica gel	<i>i</i> -Pr <sub>2</sub> O/HForm/w (90:7:3)	43
	Silica gel G	EtOH/NH <sub>3</sub> /THF	30
Diols (see Alcohols, polyhydric)			
Disulfides	Alumina	Hex	57
Disulfides, 3,5-dinitro-benzoates	Whatman 3 (impregnated with 10% paraffin oil in (CH <sub>2</sub> ) <sub>6</sub> )	DMF/MeOH/w or Foram/MeOH/w	58
Flavinoids	Paper	<i>n</i> -BuOH/AcOH/w or EtOAc/w or AcOH/w or C <sub>6</sub> H <sub>6</sub> /AcOH/w	60
	Polyamide	MeOH/H <sub>2</sub> O	3
	Silica gel	C <sub>6</sub> H <sub>6</sub> /Py/AcOH (36:9:5)	59
		Petet/EtOAc (2:1)	
	Silica gel (impregnated with NaAc)	Tol/EtForm/HFor (5:4:1)	3
	Silicic acid (starch bound)	EtOAc/Skellysolve B	3
Glycerides	Silica gel G	CHCl <sub>3</sub> /C <sub>6</sub> H <sub>6</sub> (7:3)	3
	Silica gel G (impregnated with silver nitrate)	CHCl <sub>3</sub> /AcOH (99.5:0.5)	3
Glycolipids	Silica gel G	<i>n</i> -PrOH/NH <sub>3</sub> (12%) (4:1)	3
Glycols, polyethylene	Paper	<i>n</i> -PrOH/EtOAc/w (7:1:2) or <i>n</i> -BuOH/AcOH/w (4:1:5) or <i>t</i> -AmOH/ <i>n</i> -PrOH/w (8:2:3) or EtOAc/AcOH/w (9:2:2)	60
	Silica gel	Ac or <i>n</i> -BuOH/AcOH/w	61
Hydroxamates	Silica gel	<i>i</i> -Pr <sub>2</sub> O or <i>i</i> -Pr <sub>2</sub> O/EtOAc (1:4) or <i>i</i> -Pr <sub>2</sub> O/ <i>i</i> -C <sub>8</sub> H <sub>18</sub>	62
Hydroxamic acids	Kieselguhr G (impregnated with diethylene glycol or triethylene glycol adipate polyesters)	<i>i</i> -Pr <sub>2</sub> O/Petet/CCl <sub>4</sub> /HForm/w (50:20:20:8:1)	98
Indoles	Acetylated (ascending)	CHCl <sub>3</sub> /MeOH/w (10:10:6)	63
	Cellulose (thin-layer)	w or HCl (0.005 <i>N</i> ) or <i>n</i> -BuOH/AcOH/w (12:3:5) or C <sub>6</sub> H <sub>6</sub> /AcOH/w (125:72:3)	64
$\alpha$ -Ketoacids	Silica gel (CaSO <sub>4</sub> impregnated)	EtOH/CHCl <sub>3</sub> /NH <sub>3</sub>	44

# Stationary and Mobile Phases (continued)

Family	Stationary Phase	Mobile Phase	Reference
Ketones, 2,4-dinitro-phenyl hydrazones	Alumina IB	MeCl or Tol/THF (4:1)	32
Lactams	Silica gel IB	MeCl or Tol/THF (4:1)	32
	Silica gel	<i>i</i> -Pr <sub>2</sub> O or <i>i</i> -Pr <sub>2</sub> O/EtOAc (1:4) or <i>i</i> -Bu <sub>2</sub> O/ <i>i</i> -C <sub>8</sub> H <sub>18</sub>	62
Lactones	Silica gel	<i>i</i> -Pr <sub>2</sub> O or <i>i</i> -Pr <sub>2</sub> O/EtOAc (1:4) or <i>i</i> -Bu <sub>2</sub> O/ <i>i</i> -C <sub>8</sub> H <sub>18</sub>	62
Lipids	Alumina	Petet/Et <sub>2</sub> O (95:5)	3
	Silica gel G	Petet/Et <sub>2</sub> O/AcOH (90:10:1)	3
	Silicic acid	CHCl <sub>3</sub> /MeOH/w (80:25:3)	3
Mercaptans (see Thiols)			
Nitrosamines	Silica gel	Hex/Et <sub>2</sub> O/MeCl	65
	Kieselgel	MeCl/Hex/Et <sub>2</sub> O (2:3:4) (aliphatic, aromatic); MeCl/Hex/Et <sub>2</sub> O (5:7:10) (cyclic)	66
Nucleotides	Cellulose	AmSO <sub>4</sub> (sat'd)/NaAc(1 M)/ <i>i</i> -PrOH (80:18:2)	3
	Cellulose (on DEAE)	HCl (aq)	3
Oximes	Silica gel G	C <sub>6</sub> H <sub>6</sub> /EtOAc or C <sub>6</sub> H <sub>6</sub> /MeOH (abs)	67
Peroxides	Silicone filter paper	w/EtOH/CHCl <sub>3</sub>	68
Phenols	Alumina	Et <sub>2</sub> O	3
	Alumina/AcOH	C <sub>6</sub> H <sub>6</sub>	3
	Silica gel A	CHCl <sub>3</sub> /AcOH (5:1) or CHCl <sub>3</sub> /Ac/AcOH (10:2:1) or C <sub>6</sub> H <sub>6</sub> /AcOH (5:1) or Petet (80°)/CCl <sub>4</sub> /AcOH (4:6:1) or CHCl <sub>3</sub> /Ac/Et <sub>2</sub> NH (4:2:0.2)	69
	Silica gel G	C <sub>6</sub> H <sub>6</sub> /Diox/AcOH (90:25:4)	3
	Silica gel/oxalic acid	C <sub>6</sub> H <sub>6</sub>	70
	Silica gel/potassium carbonate	MeCl/EtOAc/Et <sub>2</sub> NH (92:5:3 or 93:5:2)	70
Phosphates, esters	Alumina	Hex/C <sub>6</sub> H <sub>6</sub> /MeOH (2:1:1) or Hex/MeOH/Et <sub>2</sub> O	71
	Kieselgel	Hex/C <sub>6</sub> H <sub>6</sub> /MeOH (2:1:1) or Hex/MeOH/Et <sub>2</sub> O	71
Phospholipids	Silica gel G	CHCl <sub>3</sub> /MeOH/w	3
Polynuclear aromatics	Alumina	CCl <sub>4</sub>	3
	Alumina	C <sub>6</sub> H <sub>6</sub> /(CH <sub>2</sub> ) <sub>6</sub> (15:85)	72
	Silica gel	Hex or CH <sub>3</sub> CHCl <sub>2</sub> or C <sub>2</sub> HCl <sub>3</sub> or CCl <sub>4</sub>	73, 74
Polypeptides	Sephadex G-25	w or NH <sub>3</sub> (0.05 M)	3
	Silica gel G	CHCl <sub>3</sub> /MeOH (9:1) or CHCl <sub>3</sub> /Ac (9:1)	3
Pyridines	Whatman 1 (descending)	<i>n</i> -BuOH/w or <i>n</i> -BuOH/w/NH <sub>3</sub> or Ac or <i>i</i> -BuOH/w or MEK/AcOH/w	75
Pyridines, quaternary salts (descending)	Whatman 1	Ac/w or AmSO <sub>4</sub> /Ph buffer (pH = 6.8)/ <i>n</i> -PrOH(2%) or <i>n</i> -PrOH	75
Purines	Silica gel	Ac/CHCl <sub>3</sub> / <i>n</i> -BuOH/NH <sub>3</sub> (25%) (3:3:4:1)	3
Pyrrole, tricarboxylic acid	Silica gel	<i>n</i> -BuOH/EtOH/NH <sub>3</sub> /w (10:10:1:1)	64
Skatoles, hydroxy	Silica gel G	<i>i</i> -Pr <sub>2</sub> O or (ClCH <sub>2</sub> ) <sub>2</sub> / <i>i</i> -Pr <sub>2</sub> NH (6:1)	76
Steroids	Alumina	CHCl <sub>3</sub> EtOH (96:4)	3
	Paper	Petet/Tol/MeOH/w or Petet/C <sub>6</sub> H <sub>6</sub> /MeOH/w	60
	Paper (impregnated with kerosene)	<i>n</i> -PrOH/w	77
	Silica gel G	EtOAc/(CH <sub>2</sub> ) <sub>6</sub> /EtOH(abs) or EtOAc/(CH <sub>2</sub> ) <sub>6</sub> or CHCl <sub>3</sub> /EtOH (abs) or C <sub>6</sub> H <sub>6</sub> /EtOH or <i>n</i> -C <sub>6</sub> H <sub>14</sub> /EtOAc or EtOAc/ <i>n</i> -C <sub>6</sub> H <sub>14</sub> /EtOH(abs)/AcOH or EtOAc/ <i>n</i> -C <sub>6</sub> H <sub>14</sub> /AcOH	78, 79 80, 81

# Stationary and Mobile Phases (continued)

Family	Stationary Phase	Mobile Phase	Reference
Sugars	Cellulose	<i>n</i> -BuOH/Py/w (6:4:3) or EtOAc/Py/w (2:1:2)	3
	Kieselguhr G (buffered with 0.02 <i>N</i> NaAc)	EtOAc/ <i>i</i> -PrOH/w	3
	Silica gel (buffered with H <sub>3</sub> BO <sub>3</sub> )	C <sub>6</sub> H <sub>6</sub> /AcOH/MeOH (1:1:3)	3
	Silica gel (impregnated with sodium bisulfite)	EtOAc/AcOH/MeOH/w (6:1:5:1) or <i>n</i> -PrOH/w (85:15) or <i>i</i> -PrOH/EtOAc/w (7:1:2) or MEK/AcOH/w (6:1:3)	3
	Silica gel G	<i>n</i> -PrOH/conc. NH <sub>3</sub> /w (6:2:1)	3
	Whatman 1 (descending, two-dimensional)	PhOH or <i>n</i> -BuOH/AcOH	82
Sugars, aldoses	Paper	EtOAc/Py/w (2:1:2) or <i>n</i> -BuOH/AcOH/w (4:1:5) or <i>n</i> -BuOH/EtOH/H <sub>2</sub> O (5:1:4) or EtOAc/AcOH/w (9:2:2) or EtOAc/AcOH/HForm/w or EtOAc/Py/NaAc (sat'd)	60
Sugars, carbamates	Whatman 1	PhOH or <i>n</i> -BuOH/AcOH	82
	Silica gel	<i>n</i> -BuOH/H <sub>3</sub> BO <sub>3</sub> (0.03 <i>M</i> ) (9:1)	
Sugars, deoxy	Whatman 1	PhOH or <i>n</i> -BuOH/AcOH	82
Sugars, ketoses	Paper	EtOAc/Py/w (2:1:2) or <i>n</i> -BuOH/AcOH/w (4:1:5) or <i>n</i> -BuOH/EtOH/H <sub>2</sub> O (5:1:4) or EtOAc/AcOH/w (9:2:2) or w/PhOH (pH = 5.5)	60
	Whatman 1	PhOH or <i>n</i> -BuOH/AcOH	82
Sulfides	Alumina	Hex	75
	Alumina	CHCl <sub>3</sub> /MeOH	96
	Silica gel	CCl <sub>4</sub> or C <sub>6</sub> H <sub>6</sub>	83
	Silica gel DF-5	Ac/C <sub>6</sub> H <sub>6</sub> or Tol/EtOAc	95
	Whatman 4 (impregnated with formamide)	C <sub>6</sub> H <sub>6</sub> or C <sub>6</sub> H <sub>6</sub> /(CH <sub>2</sub> ) <sub>6</sub>	84
Sulfilimines, <i>p</i> -nitrosobenzene sulfonyl			
Sulfonamides	Kieselguhr	CHCl <sub>3</sub> /MeOH (9:1) or CHCl <sub>3</sub> /MeOH/NH <sub>3</sub>	85
	Silica gel	Et <sub>2</sub> O or CHCl <sub>3</sub> /MeOH (10:1)	86
	Silica gel (neutral)	<i>n</i> -BuOH/MeOH/Ac/Et <sub>2</sub> NH (9:1:1:1)	87
Sulfones	Silica gel G	CHCl <sub>3</sub> /EtOH/ <i>n</i> -C <sub>7</sub> H <sub>16</sub>	3
	Alumina	Et <sub>2</sub> O or Hex/Ac (1:1)	57
	Silica gel DF-5	Ac/C <sub>6</sub> H <sub>6</sub> or Tol/EtOAc	95
Sulfones, esters	Alumina	Et <sub>2</sub> O or Hex/Ac (1:1)	57
Sulfones, hydroxyethyl	Alumina	Hex/w (1:3)	57
Sulfoxides	Alumina	C <sub>6</sub> H <sub>6</sub> /Py (20:1) and Diox	88
	Alumina	Ac/CCl <sub>4</sub> (1:4)	97
	Silica gel	Ac or EtOAc or CHCl <sub>3</sub> /Et <sub>2</sub> O	83
	Silica gel DF-5	Ac/C <sub>6</sub> H <sub>6</sub> or Tol/EtOAc	95
	Whatman 1	PhOH/w (8:3) or <i>n</i> -BuOH/AcOH/w (9:1:2.5)	89
Sulfoxides, hydroxyethyl	Alumina	Et <sub>2</sub> O or Hex/Ac (1:1) or Hex/Et <sub>2</sub> O (1:3)	57
Terpenes	Alumina	C <sub>6</sub> H <sub>6</sub> or C <sub>6</sub> H <sub>6</sub> /Petet or C <sub>6</sub> H <sub>6</sub> /EtOH	3
	Silica gel G	<i>i</i> -Pr <sub>2</sub> O or <i>i</i> -Pr <sub>2</sub> O/Ac	3
	Silica gel/gypsum	CHCl <sub>3</sub> /C <sub>6</sub> H <sub>6</sub> (1:1)	90
	Silicic acid (starch bond)	<i>n</i> -C <sub>6</sub> H <sub>14</sub> /EtOAc (85:15)	3
Thiobarbiturates	Paper	<i>n</i> -AmOH/ <i>n</i> -BuOH/25% NH <sub>3</sub> (2:2:1)	91
Thiolactones	Silica gel	<i>i</i> -Pr <sub>2</sub> O or <i>i</i> -Pr <sub>2</sub> O/EtOAc (1:4) or <i>i</i> -Bu <sub>2</sub> O/ <i>i</i> -C <sub>8</sub> H <sub>18</sub>	62

### Stationary and Mobile Phases (continued)

Family	Stationary Phase	Mobile Phase	Reference
Thiols	Alumina	Hex	57
	Alumina (activated)	AcOH/MeCN (3:1)	96
	Alumina (5% cetane impregnated)	AcOH/MeCN (3:1)	96
	Silica gel	EtOAc or CHCl <sub>3</sub>	83
Thiophenes	Alumina G	Petlet (40–60°C)	92
	Silica gel	MeOH or C <sub>6</sub> H <sub>6</sub> /CHCl <sub>3</sub> (9:1)	92
Thiophosphate, esters		Petlet or C <sub>6</sub> H <sub>6</sub> /CHCl <sub>3</sub> or Ac or EtOH or EtOAc or MeOH	93
Ureas	Acetylated plates	CCl <sub>4</sub> /EtOAc/EtOH (100:5:2)	94
	Silica gel	CCl <sub>4</sub> /MeCl/EtOAc/HOAc (70:50:15:10)	94
Urethanes (see Ureas)			



## TYPICAL STATIONARY AND MOBILE PHASE SYSTEMS USED IN THE SEPARATION OF VARIOUS INORGANIC IONS

The following table lists a series of stationary and mobile systems that are used in the separation of various inorganic ions.<sup>1-8</sup> The list is far from detailed; consult the given references for details.

### REFERENCES

1. Kirchner, J.G., *Thin Layer Chromatography*, 2nd ed., Wiley Interscience, New York, 1978.
2. Bobbitt, J.M., *Thin Layer Chromatography*, Reinhold, New York, 1963.
3. Randerath, K., *Thin Layer Chromatography*, Academic Press, New York, 1963.
4. Randerath, K., *Thin Layer Chromatography*, 2nd ed., Verlag, Chemie, Weinheim, Germany, 1975.
5. Gagliardi, E. and Brodar, B., Thin-layer chromatography of metals on cellulose. Behavior of Group IIIB in the halogenic acid-alcohol system, *Chromatographia*, 2, 267, 1969.
6. Gagliardi, E. and Brodar, B., Thin layer chromatography of metals on cellulose. II. Behaviour of group IA, IIA, IVB, VB and VIB in the system halogen acid-alcohol, *Chromatographia*, 3, 7, 1970.
7. Gagliardi, E. and Brodar, B., Thin layer chromatography of metals on cellulose. III. Behavior of the transition metals in the system halogen acid-alcohol, *Chromatographia*, 3, 320, 1970.
8. MacDonald, J.C., Ed., *Inorganic Chromatographic Analysis*, John Wiley & Sons, New York, 1985.

**Typical Stationary and Mobile Phase Systems Used in the Separation of Various Inorganic Ions**

Stationary Phase	Mobile Phase	Solvent Ratio	Separated Ions
Silica gel G	Butanol/1.5 N HCl/2,5-hexanedione	100:20:0.5	Hydrogen sulfide group
Silica gel G	Acetone/conc. HCl/2,5-hexanedione	100:1:0.5	Ammonium sulfide group
Silica gel G	Water sat'd ethyl acetate/tributyl phosphate	100:4	U, Ga, Al
Silica gel G	Ethanol/acetic acid	100:1	Alkali metals
Silica gel G	Acetone/1-butanol/conc. NH <sub>4</sub> OH/water	65:25:10:5	Halogens
Silica gel G	Methanol/conc. NH <sub>4</sub> OH/10% trichloroacetic acid/water	50:15:5:30	Phosphates
Dowex 1-cellulose (1:1)	1 M aqueous sodium nitrate		Halogens
Cellulose	HCl (or HBr)/alcohol mixtures	Variable	Groups IA, IIA, IIIB, IVB, VB, VIB, transition metals
Cellulose	1-Butanol/water/HCl	8:1:1	Fe, Al, Ga, Ti, In
Cellulose	Acetic acid/pyridine/conc. HCl	80:6:20	Ammonium sulfide group
DEAE cellulose	Sodium azide/HCl	Variable	Cd, Cu, Hg
Amberlite CG 400 and CG 120	HCl/HNO <sub>3</sub> , conc.	Variable	Pb, Bi, Sn, Sb, Cu, Cr, Hg

sat'd = saturated

conc. = concentrated

## SPRAY REAGENTS IN THIN-LAYER CHROMATOGRAPHY

The following table lists the most popular spray reagents needed to identify organic compounds on chromatographic plates. These reagents have been thoroughly covered in several books<sup>1-3</sup> and reviews.<sup>4-23</sup> Due to the aerosol nature of the spray and the chemical hazards associated with several of these chemicals, the use of a fume hood is highly recommended. The original references of the spray reagents are given to provide information about their results with individual compounds.<sup>24-138</sup> A list and description of some complicated protocols follow this section of the chapter. (Note: 1  $\gamma$  = 1  $\mu\text{g}/\text{cm}^2$  on a TLC plate.)

## REFERENCES

1. Krebs, K.G., Heusser, D., and Wimmer, H., Spray reagents, in *Thin Layer Chromatography, A Laboratory Handbook*, Stahl, E., Ed., Springer-Verlag, New York, 1969, p. 854.
2. Bobbitt, J.B., Visualization, in *Thin Layer Chromatography*, Reinhold, New York, 1963, chap. 7.
3. Touchstone, J.C., Visualization procedures, in *Techniques and Application of Thin Layer Chromatography*, John Wiley & Sons, New York, 1985, p. 172.
4. Pataki, G., Paper, thin-layer, and electrochromatography of aminoacids in biological material, *Z. Klin. Chem.*, 2, 129, 1964; *Chem. Abs.*, 64, 5425c, 1966.
5. Padley, F.B., Thin-layer chromatography of lipids, *Thin-Layer Chromatography Proceedings Symposium, Rome 1963*, Marini-BéHob, G.B., Elsevier, New York, 1964, p. 87.
6. Honjo, M., Thin-layer chromatography of nucleic acid derivatives, *Kagaku No Ryoiki Zokan*, 64, 1, 1964.
7. Kazumo, T., Thin-layer chromatography of bile acids, *Kagaku No Ryoiki Zokan*, 64, 19, 1964.
8. Nakazawa, Y., Thin-layer chromatography of compound lipids, *Kagaku No Ryoiki Zokan*, 64, 31, 1964.
9. Nishikaze, O., Separation and quantitative analysis of adrenocortical hormone and its metabolite ( $\text{C}_{21}$ ) by thin-layer chromatography, *Kagaku No Ryoiki Zokan*, 64, 37, 1964.
10. Shikita, M., Kazikazi, H., and Tamaoki, B., Thin-layer chromatography of radioactive substances, *Kagaku No Ryoiki Zokan*, 64, 45, 1964.
11. Mo, I. and Hashimoto, Y., Method of thin-layer zone electrophoresis, *Kagaku No Ryoiki Zokan*, 64, 61, 1964.
12. Kinoshita, S., Thin-layer chromatography of sugar esters, *Kagaku No Ryoiki Zokan*, 64, 79, 1964.
13. Okada, M., Thin-layer chromatography of cardiotonic glycosides, *Kagaku No Ryoiki Zokan*, 64, 103, 1964.
14. Omoto, T., Thin-layer chromatography of toad toxin, *Kagaku No Ryoiki Zokan*, 64, 115, 1964.
15. Furnya, C. and Itokawa, H., Thin-layer chromatography of triterpenoids, *Kagaku No Ryoiki Zokan*, 64, 123, 1964.
16. Zenda, H., Thin-layer chromatography of aconitine-type alkaloids, *Kagaku No Ryoiki Zokan*, 64, 133, 1964.
17. Hara, S. and Tanaka, H., Thin-layer chromatography of mixed pharmaceutical preparations, *Kagaku No Ryoiki Zokan*, 64, 141, 1964.
18. Katsui, G., Thin-layer chromatography of vitamins, *Kagaku No Ryoiki Zokan*, 64, 157, 1964.
19. Fujii, S. and Kamikura, M., Thin-layer chromatography of pigments, *Kagaku No Ryoiki Zokan*, 64, 173, 1964.
20. Hosogai, Y., Thin-layer chromatography of organic chlorine compounds, *Kagaku No Ryoiki Zokan*, 64, 185, 1964.
21. Takeuchi, T., Thin-layer chromatography of metal complex salts, *Kagaku No Ryoiki Zokan*, 64, 197, 1964.
22. Yamakawa, H. and Tanigawa, K., Thin-layer chromatography of organic metal compounds, *Kagaku No Ryoiki Zokan*, 64, 209, 1964.
23. Ibayashi, H., Thin-layer chromatography of steroid hormones and its clinical application, *Kagaku No Ryoiki Zokan*, 64, 227, 1964.

24. Beckett, A.H., Beavan, M.A., and Robinson, A.E., Paper chromatography: multiple spot formation by sympathomimetic amines in the presence of acids, *J. Pharm. Pharmacol.*, 12, 203T, 1960; *Chem. Abs.*, 55, 9785c, 1961.
25. Heacock, R.A. and Scott, B.D., The chemistry of the "aminochromes." Part IV. Some new aminochromes and their derivatives, *Can. J. Chem.*, 38, 516, 1960.
26. Matthews, J.S., Steroids (CCXXIII) color reagent for steroids in thin-layer chromatography, *Biochim. Biophys. Acta*, 69, 163, 1963; *Chem. Abs.*, 58, 14043d, 1963.
27. Wasicky, R. and Frehden, O., Spot-plate tests in the examination of drugs. I. Aldehyde and amine tests for the recognition of ethereal oils, *Mikrochim. Acta*, 1, 55, 1937; *Chem. Abs.*, 31, 5944, 1937.
28. Lane, E.S., Thin-layer chromatography of long-chain tertiary amines and related compounds, *J. Chromatogr.*, 18, 426, 1965; *Chem. Abs.*, 63, 7630f, 1965.
29. Neu, R., A new color method for determining alkaloids and organic bases with sodium tetraphenylborate, *J. Chromatogr.*, 11, 364, 1963; *Chem. Abs.*, 59, 12181d, 1963.
30. Zinser, M. and Baumgartel, C., Thin-layer chromatography of ergot alkaloids, *Arch. Pharm.*, 297, 158, 1964; *Chem. Abs.*, 60, 13095f, 1964.
31. Ashworth, M.R.F. and Bohnstedt, G., Reagent for the detection and determination of N-active hydrogen, *Talanta*, 13, 1631, 1966.
32. Whittaker, V.P. and Wijesundera, S., Separation of esters of choline, *Biochem. J.*, 51, 348, 1952; *Chem. Abs.*, 46, 7940g, 1952.
33. Heacock, R.A. and Mahon, M.E., The color reactions of the hydroxyskatoles, *J. Chromatogr.*, 17, 338, 1965; *Chem. Abs.*, 62, 13824g, 1965.
34. Micheel, F. and Schweppe, H., Paper chromatographic separation of hydrophobic compounds with acetylated cellulose paper, *Mikrochim. Acta*, 53, 1954; *Chem. Abs.*, 48, 4354i, 1954.
35. Smyth, R.B. and Mckeown, G.G., Analysis of arylamines and phenols in oxidation-type hair dyes by paper chromatography, *J. Chromatogr.*, 16, 454, 1964; *Chem. Abs.*, 62, 8930e, 1963.
36. Kawerau, E. and Wieland, T., Aminoacids chromatograms, *Nature*, 168, 77, 1951; *Chem. Abs.*, 46, 382h, 1952.
37. Sturm, A. and Scheja, H.W., Separation of phenolic acids by high voltage electrophoresis, *J. Chromatogr.*, 16, 194, 1964; *Chem. Abs.*, 62, 6788b, 1965.
38. Feigl, F., *Spot Tests in Organic Analysis*, 7th ed., Elsevier, Amsterdam, Holland, 1966, p. 251.
39. Curzon, G. and Giltrow, J., A chromatographic color reagent for a group of aminoacids, *Nature*, 172, 356, 1953.
40. Heacock, R.A., Nerenberg, C., and Payza, A.N., The chemistry of the "aminochromes." Part I. The preparation and paper chromatography of pure adrenochrome, *Can. J. Chem.*, 36, 853, 1958.
41. Heacock, R.A., The aminochromes, in *Advances in Heterocyclic Chemistry*, Katritsky, A.R., Ed., Academic Press, New York, 1965, p. 205; *Chem. Abs.*, 65, 5432d, 1966.
42. Wieland, T. and Bauer, L., Separation of purines and aminoacids, *Angew. Chem.*, 63, 511, 1951; *Chem. Abs.*, 46, 1082h, 1952.
43. Hara, S. and Takeuchi, M., Systematic analysis of bile acids and their derivatives by thin layer chromatography, *J. Chromatogr.*, 11, 565, 1963; *Chem. Abs.*, 60, 838f, 1964.
44. Anthony, W.L. and Beher, W.T., Color detection of bile acids using thin layer chromatography, *J. Chromatogr.*, 13, 570, 1964; *Chem. Abs.*, 60, 13546c, 1964.
45. Hauck, A., Detection of caffeine by paper chromatography, *Deut. Z. Gerichtl. Med.*, 54, 98, 1963; *Chem. Abs.*, 60, 838b, 1964.
46. Suryaraman, M.G. and Cave, W.T., Detection of some aliphatic saturated long chain hydrocarbon derivatives by thin-layer chromatography, *Anal. Chim. Acta*, 30, 96, 1964; *Chem. Abs.*, 60, 7463e, 1964.
47. Passera, C., Pedrotti, A., and Ferrari, G., Thin-layer chromatography of carboxylic acids and ketoacids of biological interest, *J. Chromatogr.*, 14, 289, 1964; *Chem. Abs.*, 60, 16191f, 1964.
48. Grant, D.W., Detection of some aromatic acids, *J. Chromatogr.*, 10, 511, 1963; *Chem. Abs.*, 59, 5772a, 1963.
49. Roux, D.G., Some recent advances in the identification of leucoanthocyanins and the chemistry of condensed tanins, *Nature*, 180, 973, 1957; *Chem. Abs.*, 52, 5212f, 1958.
50. Abbott, D.C., Egan, H., and Thompson, J., Thin-layer chromatography of organochlorine pesticides, *J. Chromatogr.*, 16, 481, 1964; *Chem. Abs.*, 62, 11090c, 1965.

51. Adamec, O., Matis, J., and Galvanek, M., Fractionation and quantitative determination of urinary 17-hydroxycorticosteroids by thin layer chromatography on silica gel, *Steroids*, 1, 495, 1963.
52. French, D., Levine, M.L., Pazur, J.H., and Norberg, E., Studies on the Schardinger dextrans: the preparation and solubility characteristics of alpha, beta and gamma dextrans, *J. Am. Chem. Soc.*, 71, 353, 1949.
53. Knappe, E. and Rohdewald, I., Thin-layer chromatography of dicarboxylic acids. V. Separation and identification of hydroxy dicarboxylic acids, of di- and tricarboxylic acids of the citrate cycle, and some other dicarboxylic acids of plant origin, *Z. Anal. Chem.*, 211, 49, 1965; *Chem. Abs.*, 63, 7333c, 1965.
54. Wright, J., Detection of humectants in tobacco by thin layer chromatography, *Chem. Ind. (London)*, 1125, 1963.
55. Toennies, G. and Kolb, J.J., Techniques and reagents for paper chromatography, *Anal. Chem.*, 23, 823, 1951; *Chem. Abs.*, 45, 8392i, 1951.
56. Kaufmann, H.P. and Sen Gupta, A.K., Terpenes as constituents of the unsaponifiables of fats, *Chem. Berl.*, 97, 2652, 1964; *Chem. Abs.*, 61, 14723b, 1964.
57. Gage, T.B., Douglass, C.D., and Wender, S.H., Identification of flavonoid compounds by filter paper chromatography, *Anal. Chem.*, 23, 1582, 1951; *Chem. Abs.*, 46, 2449c, 1952.
58. Hörhammer, L., Wagner, H., and Hein, K., Thin layer chromatography of flavonoids on silica gel, *J. Chromatogr.*, 13, 235, 1964; *Chem. Abs.*, 60, 13856c, 1964.
59. Nakamura, H. and Pisano, J.J., Specific detection of primary catecholamines and their 3-O-methyl derivatives on thin-layer plates using a fluorogenic reaction with fluorecamine, *J. Chromatogr.*, 154, 51, 1978; *Chem. Abs.*, 89, 117958x, 1978.
60. Neu, R., Analyses of washing and cleaning agents. XVIII. A new test for polyethylene glycols and their esters, *Chem. Abs.*, 49, 16475c, 1955; *Chem. Abs.*, 54, 2665e, 1960.
61. Korte, F. and Vogel, J., Thin-layer chromatography of lactones, lactams and thiolactones, *J. Chromatogr.*, 9, 381, 1962; *Chem. Abs.*, 58, 9609c, 1963.
62. Harley-Mason, J. and Archer, A.A.P.G., p-Dimethylamino-cinnamaldehyde as a spray reagent for indole derivatives on paper chromatograms, *Biochem. J.*, 69, 60, 1958; *Chem. Abs.*, 52, 18600g, 1958.
63. Heacock, R.A. and Mahon, M.E., Paper chromatography of some indole derivatives on acetylated paper, *J. Chromatogr.*, 6, 91, 1961.
64. Adams, C.W.M., A perchloric acid-naphthoquinone method for the histochemical localization of cholesterol, *Nature*, 192, 331, 1961.
65. Bennet-Clark, T.A., Tamblah, M.S., and Kefford, N.P., Estimation of plant growth substances by partition chromatography, *Nature*, 169, 452, 1951; *Chem. Abs.*, 46, 6181c, 1952.
66. Gordon, S.A. and Weber, R.P., Estimation of indole acetic acid, *Plant Physiol.*, 26, 192, 1951; *Chem. Abs.*, 45, 4605c, 1951.
67. Dickmann, S.R. and Crockett, A.L., Reactions of xanthidrol. IV. Determination of tryptophan in blood plasma and proteins, *J. Biol. Chem.*, 220, 957, 1956; *Chem. Abs.*, 49, 7028h, 1956.
68. Mangold, H.K., Lamp, B.G., and Schlenk, H., Indicators for the paper chromatography of lipids, *J. Am. Chem. Soc.*, 77, 6070, 1953; *Chem. Abs.*, 50, 5074f, 1956.
69. Witter, R.F., Marinetti, G.V., Morrison, A., and Heicklin, L., Paper chromatography of phospholipids with solvent mixtures of ketones and acetic acid, *Arch. Biochem. Biophys.*, 68, 15, 1957; *Chem. Abs.*, 51, 12200a, 1957.
70. Martin, H.P., Reversed phase paper chromatography and detection of steroids of the cholesterol class, *Biochim. Biophys. Acta*, 25, 408, 1957.
71. Preussmann, R., Daiber, D., and Hengy, H., Sensitive color reaction for nitrosamines on thin-layer chromatography, *Nature*, 201, 502, 1964; *Chem. Abs.*, 60, 12663e, 1964.
72. Preussmann, R., Neurath, G., Wulf-Lorentzen, G., Daiber, D., and Hengy, H., Color formation and thin-layer chromatography of N-nitrosocompounds, *Z. Anal. Chem.*, 202, 187, 1964.
73. Hranisavljevic-Jakovljevic, M., Pejkoivic-Tadic, I., and Stojiljkovic, A., Thin-layer chromatography of isomeric oximes, *J. Chromatogr.*, 12, 70, 1963; *Chem. Abs.*, 60, 7d, 1964.
74. Abraham, M.H., Davies, A.G., Llewellyn, D.R., and Thain, E.M., Chromatographic analysis of organic peroxides, *Anal. Chem. Acta*, 17, 499, 1957; *Chem. Abs.*, 53, 120b, 1959.
75. Knappe, E. and Peteri, D., Thin-layer chromatographic identification of organic peroxides, *Z. Anal. Chem.*, 190, 386, 1962; *Chem. Abs.*, 58, 5021a, 1963.

76. Servigne, Y. and Duval, C., Paper chromatographic separation of mineral anions containing sulfur, *Comput. Rend.*, 245, 1803, 1957; *Chem. Abs.*, 52, 5207b, 1958.
77. Lisboa, B.P., Characterization of  $\Delta^4$ -3-oxo- $C_{21}$ -steroids on thin-layer chromatography, *J. Chromatogr.*, 16, 136, 1964; *Chem. Abs.*, 62, 3409, 1965.
78. Sherma, J. and Hood, L.V.S., Thin-layer solubilization chromatography. I. Phenols, *J. Chromatogr.*, 17, 307, 1965; *Chem. Abs.*, 62, 13819b, 1965.
79. Gumprecht, D.L., Paper chromatography of some isomeric monosubstituted phenols, *J. Chromatogr.*, 18, 336, 1965; *Chem. Abs.*, 63, 7630h, 1965.
80. Barton, G.M.,  $\alpha,\alpha$ -Dipyridyl as a phenol-detecting reagent, *J. Chromatogr.*, 20, 189, 1965; *Chem. Abs.*, 64, 2724a, 1966.
81. Sajid, H., Separation of chlorinated cresols and chlorinated xylenols by thin-layer chromatography, *J. Chromatogr.*, 18, 419, 1965; *Chem. Abs.*, 63, 7630d, 1965.
82. Seeboth, H., Thin-layer chromatography analysis of phenols, *Monatsber. Deut. Akad. Wiss. Berl.*, 5, 693, 1963; *Chem. Abs.*, 61, 2489c, 1964.
83. Burke, W.J., Potter, A.D., and Parkhurst, R.M., Neutral silver nitrate as a reagent in the chromatographic characterization of phenolic compounds, *Anal. Chem.*, 32, 727, 1960; *Chem. Abs.*, 54, 13990d, 1960.
84. Perifoy, P.V., Slaymaker, S.C., and Nager, M., Tetracyanoethylene as a color-developing reagent for aromatic hydrocarbons, *Anal. Chem.*, 31, 1740, 1959; *Chem. Abs.*, 54, 5343e, 1960.
85. Bate-Smith, E.C., and Westall, R.G., Chromatographic behavior and chemical structure (I) naturally occurring phenolic substances, *Biochem. Biophys. Acta*, 4, 427, 1950; *Chem. Abs.*, 44, 5677a, 1950.
86. Noifalisse, A. and Grosjean, M.H., Detection of phenothiazine derivatives by thin-layer chromatography, *J. Chromatogr.*, 16, 236, 1964; *Chem. Abs.*, 62, 10295f, 1965.
87. Schreiber, K., Aurich, O., and Osske, G., Solanum alkaloids. XVIII. Thin-layer chromatography of Solanum steroid alkaloids and steroidal sapogenins, *J. Chromatogr.*, 12, 63, 1963; *Chem. Abs.*, 60, 4442h, 1964.
88. Clarke, E.G.C., Identification of solanine, *Nature*, 181, 1152, 1958; *Chem. Abs.*, 53, 7298h, 1959.
89. Donner, R. and Lohs, K., Cobalt chloride in the detection of organic phosphate ester by paper and especially thin-layer chromatography, *J. Chromatogr.*, 17, 349, 1965; *Chem. Abs.*, 62, 13842d, 1965.
90. Kucharczyk, N., Fohl, J., and Vymetal, J., Thin-layer chromatography of aromatic hydrocarbons and some heterocyclic compounds, *J. Chromatogr.*, 11, 55, 1963; *Chem. Abs.*, 59, 9295g, 1963.
91. Kodicek, E. and Reddi, K.K., Chromatography of nicotinic acid derivatives, *Nature*, 168, 475, 1951; *Chem. Abs.*, 46, 3601g, 1952.
92. Hodgson, E., Smith, E., and Guthrie, F.E., Two-dimensional thin-layer chromatography of tobacco alkaloids and related compounds, *J. Chromatogr.*, 20, 176, 1965; *Chem. Abs.*, 64, 3960b, 1966.
93. Stevens, P.J., Thin-layer chromatography of steroids: specificity of two location reagents, *J. Chromatogr.*, 14, 269, 1964; *Chem. Abs.*, 61, 2491b, 1964.
94. Lisboa, B.P., Application of thin-layer chromatography to the steroids of the androstane series, *J. Chromatogr.*, 13, 391, 1964; *Chem. Abs.*, 60, 13890b, 1964.
95. Lisboa, B.P., Separation and characterization of  $\Delta^5$ -3-hydroxy- $C_{19}$ -steroids by thin-layer chromatography, *J. Chromatogr.*, 19, 333, 1965; *Chem. Abs.*, 63, 16403h, 1965.
96. Lisboa, B.P., Thin-layer chromatography of  $\Delta^4$ -3-oxosteroids of the androstane series, *J. Chromatogr.*, 19, 81, 1965; *Chem. Abs.*, 63, 13619e, 1965.
97. Neher, R. and Wettstein, A., Steroids (CVII) color reactions: corticosteroids in the paper chromatogram, *Helv. Chim. Acta*, 34, 2278, 1951; *Chem. Abs.*, 46, 3110d, 1952.
98. Michalec, C., Paper chromatography of cholesterol and cholesterol esters, *Naturwissenschaften*, 42, 509, 1955; *Chem. Abs.*, 51, 5884a, 1957.
99. Scheidegger, J.J. and Cherbuliez, E., Hederacoside A, a heteroside extracted from English ivy, *Helv. Chim. Acta*, 38, 547, 1955; *Chem. Abs.*, 50, 1685g, 1956.
100. Richter, E., Detection of sterols with naphthoquinone-perchloric acid on silica gel layers, *J. Chromatogr.*, 18, 164, 1965; *Chem. Abs.*, 63, 7653a, 1965.
101. Lisboa, B.P., Thin-layer chromatography of steroids, *J. Pharm. Belg.*, 20, 435, 1965; *Chem. Abs.*, 65, 570c, 1966.
102. Adachi, S., Thin-layer chromatography of carbohydrates in the presence of bisulfite, *J. Chromatogr.*, 17, 295, 1965; *Chem. Abs.*, 62, 13818g, 1965.



103. Bryson, J.L. and Mitchell, T.J., Spraying reagents for the detection of sugar, *Nature*, 167, 864, 1951; *Chem. Abs.*, 45, 8408b, 1951.
104. Sattler, L. and Zerban, F.W., Limitations of the anthrone test for carbohydrates, *J. Am. Chem. Soc.*, 72, 3814, 1950; *Chem. Abs.*, 45, 1039b, 1951.
105. Bacon, J.S.D. and Edelmans, J., Carbohydrates of the Jerusalem artichoke and other compositae, *Biochem. J.*, 48, 114, 1951; *Chem. Abs.*, 45, 5242b, 1951.
106. Timell, T.E., Glaudemans, C.P.J., and Currie, A.L., Spectrophotometric method for determination of sugars, *Anal. Chem.*, 28, 1916, 1956.
107. Hay, G.W., Lewis, B.A., and Smith, F., Thin-film chromatography in the study of carbohydrates, *J. Chromatogr.*, 11, 479, 1963; *Chem. Abs.*, 60, 839b, 1964.
108. Edward, J.T. and Waldron, D.M., Detection of deoxy sugars, glycols and methyl pentoses, *J. Chem. Soc.*, 3631, 1952; *Chem. Abs.*, 47, 1009h, 1953.
109. Johanson, R., New specific reagent for keto-sugars, *Nature*, 172, 956, 1953.
110. Adachi, S., Use of dimedon for the detection of keto sugars by paper chromatography, *Anal. Biochem.*, 9, 224, 1964; *Chem. Abs.*, 61, 13616g, 1964.
111. Sattler, L. and Zerban, F.W., New spray reagents for paper chromatography of reducing sugars, *Anal. Chem.*, 24, 1862, 1952; *Chem. Abs.*, 47, 1543d, 1953.
112. Bailey, R.W. and Bourne, E.J., Color reactions given by sugars and diphenylamine-aniline spray reagents on paper chromatograms, *J. Chromatogr.*, 4, 206, 1960; *Chem. Abs.*, 55, 4251c, 1961.
113. Buchan, J.L. and Savage, R.J., Paper chromatography of starch-conversion products, *Analyst*, 77, 401, 1952; *Chem. Abs.*, 48, 8568c, 1954.
114. Schwimmer, S. and Bevenue, A., Reagent for differentiation of 1,4- and 1,6-linked glucosaccharides, *Science*, 123, 543, 1956; *Chem. Abs.*, 50, 8376a, 1956.
115. Partridge, S.M., Aniline hydrogen phthalate as a spraying reagent for chromatography of sugars, *Nature*, 164, 443, 1949.
116. Grossert, J.S. and Langer, R.F., A new spray reagent for organosulfur compounds, *J. Chromatogr.*, 97, 83, 1974; *Chem. Abs.*, 82, 25473n, 1976.
117. Snegotskii, V.I. and Snegotskaya, V.A., Thin-layer chromatography of sulfur compounds, *Zavod. Lab.*, 35, 429, 1969; *Chem. Abs.*, 71, 23436b, 1969.
118. Fishbein, L. and Fawkes, J., Detection and thin-layer chromatography of sulfur compounds. I. Sulfoxides, sulfones and sulfides, *J. Chromatogr.*, 22, 323, 1966; *Chem. Abs.*, 65, 6281e, 1966.
119. Svoronos, P.D.N., On the Synthesis and Characteristics of Sulfonyl Sulfilimines Derived from Aromatic Sulfides, Dissertation, Georgetown University, Washington, D.C., 1980 (available from University Microfilms, Order 8021272).
120. Petranek, J. and Vecera, M., Identification of organic compounds. XXIV. Separation and identification of sulfides by paper chromatography, *Chem. Listy*, 52, 1279, 1958; *Chem. Abs.*, 53, 8039d, 1958.
121. Bican-Fister, T. and Kajganovic, V., Quantitative analysis of sulfonamide mixtures by thin-layer chromatography, *J. Chromatogr.*, 16, 503, 1964; *Chem. Abs.*, 62, 8943d, 1965.
122. Bratton, A.C. and Marshall, E.K., Jr., A new coupling component for sulfanilamide determination, *J. Biol. Chem.*, 128, 537, 1939.
123. Borecky, J., Pinakryptol yellow, reagent for the identification of arenesulfonic acids, *J. Chromatogr.*, 2, 612, 1959; *Chem. Abs.*, 54, 16255a, 1960.
124. Pollard, F.H., Nickless, G., and Burton, K.W.C., A spraying reagent for anions, *J. Chromatogr.*, 8, 507, 1962; *Chem. Abs.*, 58, 3873b, 1963.
125. Coyne, C.M. and Maw, G.A., Paper chromatography for aliphatic sulfonates, *J. Chromatogr.*, 14, 552, 1964; *Chem. Abs.*, 61, 7679d, 1964.
126. Wolski, T., Color reactions for the detection of sulfoxides, *Chem. Anal. (Warsaw)*, 14, 1319, 1969; *Chem. Abs.*, 72, 106867q, 1970.
127. Suchomelova, L., Horak, V., and Zyka, J., The detection of sulfoxides, *Microchem. J.*, 9, 196, 1965; *Chem. Abs.*, 63, 9062a, 1965.
128. Thompson, J.F., Arnold, W.N., and Morris, C.J., A sensitive qualitative test for sulfoxides on paper chromatograms, *Nature*, 197, 380, 1963; *Chem. Abs.*, 58, 7351d, 1963.
129. Karaulova, E.N., Bobruiskaya, T.S., and Gal'pern, G.D., Thin-layer chromatography of sulfoxides, *Zh. Analit. Khim.*, 21, 893, 1966; *Chem. Abs.*, 65, 16046f, 1966.

130. Bergstrom, G. and Lagercrantz, C., Diphenylpicrylhydrazyl as a reagent for terpenes and other substances in thin-layer chromatography, *Acta Chem. Scand.*, 18, 560, 1964; *Chem. Abs.*, 61, 2491h, 1964.
131. Urx, M., Vondrackova, J., Kovarik, L., Horsky, O., and Herold, M., Paper chromatography of tetracyclines, *J. Chromatogr.*, 11, 62, 1963; *Chem. Abs.*, 59, 9736g, 1963.
132. Dietz, W. and Soehring, K., Identification of thiobarbituric acids in urine by paper chromatography, *Arch. Pharm.*, 290, 80, 1957; *Chem. Abs.*, 52, 4736d, 1958.
133. Prinzler, H.W., Pape, D., Tauchmann, H., Teppke, M., and Tzcharnke, C., Thin-layer chromatography of organic sulfur compound, *Ropa Uhlie*, 8, 13, 1966; *Chem. Abs.*, 65, 9710h, 1966.
134. Curtis, R.F. and Philips, G.T., Thin-layer chromatography of thiophene derivatives, *J. Chromatogr.*, 9, 366, 1962; *Chem. Abs.*, 58, 10705c, 1963.
135. Salame, M., Detection and separation of the most important organo-phosphorus pesticides by thin-layer chromatography, *J. Chromatogr.*, 16, 476, 1964; *Chem. Abs.*, 62, 11090b, 1965.
136. Siliprandi, D. and Siliprandi, M., Separation and determination of phosphate esters of thiamine, *Biochem. Biophys. Acta*, 14, 52, 1954; *Chem. Abs.*, 49, 6036f, 1955.
137. Nuernberg, E., Thin-layer chromatography of vitamins, *Deut. Apotheker-Zfg.*, 101, 268, 1961; *Chem. Abs.*, 60, 372, 1964.
138. Mariani, A. and Vicari, C., Determination of vitamin D in the presence of interfering substances, *Chem. Abs.*, 60, 373a, 1964.

#### Spray Reagents in Thin-Layer Chromatography

Family/ Functional Group	Test	Result	Reference
Adrenaline (and derivatives)	2,6-Dichloroquinonechloroimide (0.5% in absolute ethanol)	Variety of colors	1
	Potassium ferricyanide (0.6% in 0.5% sodium hydroxide)	Red spots	25
Adrenochromes	4- <i>N,N</i> - Dimethylaminocinnamaldehyde	Blue-green to gray-green spots	26
	Ehrlich reagent	Blue-violet to red-violet spots	26
	Zinc acetate (20%)	Blue or yellow fluorescent spots	26
Alcohols	Ceric ammonium sulfate (or nitrate)	Yellow/green spots on red background	1, 3
	2,2-Diphenylpicrylhydrazyl (0.06% in chloroform)	Yellow spots on purple background after heating (110°C, 5 min)	3
	Vanillin (1% in conc. sulfuric acid)	Variety of spots after heating (120°C) — good only for higher alcohols	27
Aldehydes	<i>o</i> -Dianisidine (saturated solution in acetic acid)	Variety of spots	28
	2,4-Dinitrophenylhydrazine	Blue colors (saturated ketones); olive green colors (saturated aldehydes); slow-developing colors (unsaturated carbonyl compounds)	1
	2,4-Diphenylpicrylhydrazyl (0.06% in chloroform)	Yellow spots on a purple background after heating (110°C, 5 min)	3
	Hydrazine sulfate (1% in 1 <i>N</i> hydrochloric acid)	Spots under UV (especially after heating)	3
	Tollen's reagent	Dark spots	1
Aldehydes, carotenoid	Rhodamine (1–5% in ethanol)	Variety of spots after treatment with strong alkali (sensitivity 0.03γ)	1
Alkaloids	Bromcresol green (0.05% in ethanol)	Green spots, especially after exposure to ammonia	3
	Chloramine-T (10% aqueous)	Rose spots after exposure to hydrochloric acid and heat	4
	Cobalt (II) thiocyanate	Blue spots on a light pink background	29
	4- <i>N,N</i> -dimethylaminobenzaldehyde (4% in 1:3 hydrochloric acid/methanol)	Characteristic spots for individual alkaloids	4

### Spray Reagents in Thin-Layer Chromatography (continued)

Family/ Functional Group	Test	Result	Reference
Alkaloids, ergot	Iodine/potassium iodide (in 2 <i>N</i> acetic acid)	Variety of spots	3
	Kalignost test	Orange/red spots fluorescing under long-wave UV	30
	Sonnenschein test	Variety of spots	1
	4- <i>N,N</i> -Dimethylaminobenzaldehyde/sulfuric acid	Blue spots	31
Amides	Chlorine/pyrazolinone/cyanide	Red spots turning blue (detection limit 0.5 µg)	32
Amines (all types unless specified)	Hydroxylamine/ferric chloride	Variety of spots	33
	Alizarin (0.1% in ethanol)	Violet spots on yellow background	3
	Chlorine/pyrazolinon/cyanide	Red spots turning blue (aromatic only)	32
	Cobalt (II) thiocyanate	Blue spots on white/pink background	29
Amines (all types unless specified) (cont.)	Diazotization and $\alpha$ -naphthol coupling	Variety of spots (1° aromatic amines only)	1
	Ehrlich reagent	Yellow spots for aromatic amines	3,4
	Fast Blue B Salt	Variety of spots (only for amines that can couple)	1
	Glucose/phosphoric acid (4%)	Variety of spots (aromatic amines only), especially after heating	35
	Malonic acid (0.2%)/salicylaldehyde (0.1%) (in ethanol)	Yellow spots after heating (120°C, 15 min)	3, 4
	1,2-Naphthoquinone-4-sulfonic acid, sodium salt (0.5% in 1 <i>N</i> acetic acid)	Variety of colors after 30 min (aromatic amines only)	36
	Ninhydrin	Red colors when exposed to ammonium hydroxide	37
	<i>p</i> -Nitroaniline, diazotized	Variety of colored spots	38
	Nitroprusside (2.5%)/acetaldehyde (5%)/sodium carbonate (1%)	Variety of spots (2° aliphatic only)	39
	Picric acid (3% in ethanol)/sodium hydroxide (10%) (5:1)	Orange spots	4
Amino acids	Potassium iodate (1%)	Variety of spots for phenylethylamines (after heating)	3
	Vanillin-potassium hydroxide	Variety of colors	40
	Dehydroascorbic acid (0.1% in 95% <i>n</i> -butanol)	Variety of colored spots	3
	2,4-Dinitrofluorobenzene	Variety of spots	1
	Isatin-zinc acetate	Variety of colors	1
	Folin reagent	Variety of colors	1
Amino alcohols	Ninhydrin	Red colors when exposed to ammonium hydroxide	36
	Vanillin/potassium hydroxide	Variety of colors	40
	Alizarin (0.1% in ethanol)	Violet on yellow background	3
	<i>p-N,N</i> -Dimethylaminocinnamaldehyde	Variety of colors	41
	Ehrlich reagent	Violet spots	26,41
	Ferric chloride (3%)	Gray-brown spots	41
Aminochromes	<i>p</i> -Nitroaniline, diazotized	Red/brown spots	26,41
	Sodium bisulfite, aqueous	Yellow fluorescence under UV	41,42
	Ninhydrin	Red colors when exposed to ammonium hydroxide	37
Aminosugars			
Ammonium salts, quaternary	Cobalt (II) thiocyanate	Variety of spots	29
Anhydrides	Hydroxylamine/ferric chloride	Variety of spots	33
Arginine	Sakaguchi reagent	Orange/red spots	1
Azulenenes	EP-reagent	Blue spots (room temperature) that fade to green/yellow shades and can be regenerated with steam	1



### Spray Reagents in Thin-Layer Chromatography (continued)

Family/ Functional Group	Test	Result	Reference
Barbiturates	Cobalt (II) nitrate (2%)/lithium hydroxide (0.5%)	Variety of colors	1
	Cupric sulfate/quinine/pyridine	Variety of colors (white, yellow, violet)	1
	s-Diphenylcarbazone (0.1% in ethanol)	Purple spots	3
	Ferrocyanide/hydrogen peroxide	Yellow/red colors	1
	Fluorescein (0.005% in 0.5 M ammonia)	Variety of spots under long- or short-wave UV	43
Bile acids	Mercurous nitrate (1%)	Variety of spots	1
	Zwicker reagent	Variety of spots	1
	Anisaldehyde/sulfuric acid	Variety of spots	4
	Antimony trichloride (in chloroform)	Variety of spots	44
	Perchloric acid (60%)	Fluorescent spots (long-wave UV) after heating (150°C, 10 min)	44
Bromides	Sulfuric acid	Variety of spots	44,45
	Fluorescein/hydrogen peroxide	Nonfluorescent spots	1
Caffeine	Chloramine-T	Pink-red spots	1
	Silver nitrate (2% in 10% sulfuric acid)	Carmine-red spots (limit 2γ)	46
Carboxylic acids	Bromocresol blue (0.5% in 0.2% citric acid)	Yellow spots on blue background	3
	Bromothymol blue (0.2% in ethanol, pH = 7)	Yellow spots upon exposure to ammonia	47
	2,6-Dichlorophenol/indophenol (0.1% in ethanol)	Red spots on blue background after heating	48
	Hydrogen peroxide (0.3%)	Blue fluorescence under long-wave UV	49
	Schweppe reagent	Dark brown spots	1
Carboxylic acids, ammonium salts			
Catechins	p-Toluenesulfonic acid (20% in chloroform)	Fluorescent spots under long-wave UV	50
Catecholamines	Ethylenediamine (50%)	Spots under short-/long-wave UV after heating (50°C, 20 min)	1
Chlorides, alkyl	2,6-Dichlorophenol indophenol (0.2%)/silver nitrate (3%) in ethanol	Variety of spots	1
	Silver nitrate (0.5% in ethanol)	Dark spots upon UV irradiation	51
	Silver nitrate/formaldehyde	Dark gray spots	1
	Silver nitrate/hydrogen peroxide	Dark spots	1
Chlorinated insecticides and pesticides	Diphenylamine (0.5%)/zinc chloride (0.5%) in acetone	Variety of colors upon heating (200°C)	1
	2-Phenoxyethanol (5%) in 0.05% silver nitrate	Variety of spots	4
	Silver nitrate/formaldehyde	Dark gray spots	1
Choline derivatives	o-Toluidine (0.5%) in ethanol	Green spots under UV (sensitivity 0.5 μg)	4
	Dipicrylamine (0.2% in 50% aqueous acetone)	Red spots on yellow background	1
Corticosteroids	Blue tetrazolium (0.05%)/sodium hydroxide (2.5 M)	Violet spots (limit 1γ/cm <sup>2</sup> )	1,52
	2,3,5-Triphenyl-H-tetrazolium chloride (2% in 0.5 NaOH)	Red spots after heating (100°C, 5 min)	1
Coumarins	Benedict reagent	Fluorescent spots under long-wave UV	1
	Potassium hydroxide (5% in methanol)	Variety of spots under long-wave UV	1
Dextrins	Iodine/potassium iodide	Blue-black spots (α-dextrins); brown-yellow spots (β- or γ-dextrins)	53

### Spray Reagents in Thin-Layer Chromatography (continued)

Family/ Functional Group	Test	Result	Reference
Dicarboxylic acids	Bromcresol purple (0.04% in basic 50% ethanol, pH = 10)	Yellow spots on blue background	4, 54
Diols (1,2-)	Lead (IV)-acetate (1% in benzene)	White spots after heating (110°C, 5 min) (limit 2 µg)	55
Disulfides	Iodine (1.3% in ethanol)/sodium azide (3.3% in ethanol)	White spots on brown iodine background	3
	Nitroprusside (sodium)	Red spots	56
Diterpenes	Antimony (III) chloride/acetic acid	Reddish yellow to blue-violet	57
Esters	Hydroxylamine/ferric chloride	Variety of spots	33
Flavonoids	Aluminum chloride	Yellow fluorescence on long-wave UV	58
	Antimony (III) chloride (10% in chloroform)	Fluorescence on long-wave UV	59
	Benedict reagent	Fluorescence on long-wave UV (only for <i>o</i> -dihydroxy compounds)	
	Lead (IV) acetate (basic, 25%)	Fluorescent spots	59
	<i>p</i> -Toluenesulfonic acid (20% in chloroform)	Fluorescent spots under long-wave UV after heating (100°C, 10 min)	4,50
Fluorescamines	Perchloric acid (70%)	Blue fluorescent spots	60
Glycols, polyethylene	Quercetin/sodium tetraphenylborate	Orange-red spots	61
Glycolipids	Diphenylamine (5% in ethanol) dissolved in 1:1 hydrochloric acid/acetic acid	Blue-gray spots	1
Glycosides, triterpene	Liebermann-Burchard	Fluorescence under long-wave UV	1
Hydroxamates	Ferric chloride (10% in acetic acid)	Brown spots	62
Hydroxamic acids	Ferric chloride (1–5% in 0.5 <i>N</i> hydrochloric acid)	Red spots	1
Imidazoles	<i>p</i> -Anisidine/amy nitrite	Red/brown spots	3
Indoles	Chlorine/pyrazolinone/cyanide	Red spots turning blue after a few minutes (limit 0.5 µg)	32
	Cinnamaldehyde/hydrochloric acid	Red spots	1
	4- <i>N,N</i> -dimethylaminocinnamaldehyde	Variety of colored spots	63
	Ehrlich reagent	Purple for indoles; blue for hydroxyindoles	9,34,64
	Ferric chloride (0.001 <i>M</i> ) in 5% perchloric acid	Red spots	3
	Naphthoquinone/perchloric acid	Orange spots	65
	Perchloric acid (5%)/ferric chloride (0.001 <i>M</i> )	Variety of colored spots	66
	Prochazka reagent	Fluorescent (yellow/orange/green) spots under long-wave UV	1
	Salkowski reagent	Variety of colored spots	67
	van Urk (or Stahl) reagent	Variety of colored spots	1
	Xyanthidrol (0.1% in acidified ethanol)	Variety of colored spots after heating (100°C)	68
Iodides	Sonnenschein test	Variety of spots	1
α-Ketoacids	2,6-Dichlorophenol/indophenol (0.1% in ethanol)	Pink spots upon heating	4,48
	<i>o</i> -Phenylenediamine (0.05% in 10% trichloroacetic acid or 0.2% in 0.1 <i>N</i> H <sub>2</sub> SO <sub>4</sub> /ethanol)	Green fluorescence under long-wave UV after heating (100°C, 2 min)	1
Ketones	<i>o</i> -Dianisidine (saturated solution in acetic acid)	Characteristic spots	28
	2,4-Dinitrophenylhydrazine	Yellow-red spots	3
Lactones	Hydroxylamine/ferric chloride	Variety of colors	33

### Spray Reagents in Thin-Layer Chromatography (continued)

Family/ Functional Group	Test	Result	Reference
Lipids	$\alpha$ -Cyclodextrin	Variety of spots (for straight-chain lipids)	53
	2',7'-Dichlorofluorescein (0.2%) in ethanol	Spots under long-wave UV	1,69
	Fluorescein	Spots after treatment with steam	1
	Rhodamine 6G (1% in acetone)	Spots under long-wave UV	70
	Tungstophosphoric acid (20% in ethanol)	Variety of colored spots after heating	71
Mercaptans (see Thiols)			
Nitro compounds	4- <i>N,N</i> -Dimethylaminobenzaldehyde/ stannous chloride/hydrochloric acid	Yellow spots	3
Nitrosamines	Diphenylamine/palladium chloride	Violet spots after exposure to short-wave UV (limit 0.5 $\gamma$ )	1,72
	Sulfanilic acid (0.5%)/ $\alpha$ -naphthylamine (0.05%) in 30% acetic acid	Spraying is preceded by short-wave UV irradiation (3 min); aliphatic nitrosamines yield red/violet spots, while aromatic ones yield green/blue spots (limit 0.2–0.5 $\gamma$ )	1,72,73
Oximes	Cupric chloride (0.5%)	Immediate green spots ( $\beta$ -oximes); green–brown spots after 10 min ( $\alpha$ -oximes)	74
Peroxides	Ammonium thiocyanate (1.2%)/ferrous sulfate (4%)	Brown–red spots	74
	<i>N,N</i> -Dimethyl- <i>p</i> -phenylene diammonium dichloride	Purple spots	76
	Ferrous thiocyanate	Red–brown spots	1,75
Persulfates	Iodide (potassium)/starch	Blue spots	1
	Benzidine (0.05% in 1 <i>N</i> acetic acid)	Blue spots	77
Phenols	Anisaldehyde/sulfuric acid	Variety of colors	1,78
	<i>p</i> -Anisidine/ammonium vanadate	Variety of spots on pink background	3
	Benzidine, diazotized	Variety of colors	79
	Ceric ammonium nitrate (46% in 2 <i>M</i> nitric acid)	Variety of spots	80
	$\alpha,\alpha'$ -Dipyridyl (0.5%)/ferric chloride (0.5%) in ethanol	Variety of spots	4,81
	Emerson	Red–orange to pink spots	1
	Fast Blue B salt	Variety of spots	1
	Ferric chloride (1–5% in 0.5 <i>N</i> HCl)	Bluish green spots	1
	Folin–Denis	Variety of spots	82
	Gibbs reagent	Variety of colors	1
	Millon reagent	Variety of colors after heating	1
	Naphthoquinone/perchloric acid	Yellow spots (phenol, catechol); dark blue spots (resorcinol)	65
	<i>p</i> -Nitroaniline, diazotized	Variety of colored spots	38
	<i>p</i> -Nitrobenzenediazonium fluoroborate	Variety of spots	84
	Silver nitrate (saturated in acetone)	Pink to deep green colors	84
	Stannic chloride (5%) in equal volumes of chloroform/acetic acid	Variety of spots after heating (100°C, 5 min)	1
	Tetracyanoethylene (10% in benzene)	Variety of colors	85
	Tollen's (or Zaffaroni) reagent	Dark spots	86
	Vanillin (1% in sulfuric acid)	Variety of colors after heating	27
	Folin–Denis reagent	Variety of spots	82
Phenols, chlorinated			
Phenothiazines	Ferric chloride (5%)/perchloric acid (20%)/nitric acid (50%) (1:9:10)	Variety of colors	4, 87

### Spray Reagents in Thin-Layer Chromatography (continued)

Family/ Functional Group	Test	Result	Reference
Phosphates, esters	Formaldehyde (0.03% in phosphoric acid)	Variety of spots	88,89
	Palladium (II) chloride (0.5% pH < 7)	Variety of spots	1
	Cobalt (II) chloride (1% in acetone or acetic acid)	Blue spots upon warming the plate at 40°C	90
Polynuclear aromatics	Formaldehyde (2%) in conc. sulfuric acid	Variety of colors	91
Purines	Tetracyanoethylene (10% in benzene)	Variety of colors	85
	Fluorescein (0.005% in 0.5 <i>M</i> ammonia)	Variety of spots under long- or short-wave UV	43
Pyrazolones	Ferric chloride (5%)/acetic acid (2 <i>N</i> ) (1:11)	Variety of colors	4
Pyridines	König reagent	Variety of spots (for free $\alpha$ -position pyridines)	92,93
Pyridines, quaternary	König reagent	Blue–white fluorescence under UV	93
Pyrimidines	Fluorescein (0.005% in 0.5 <i>M</i> ammonia)	Variety of spots under long- or short-wave UV	43
Pyrones ( $\alpha$ - and $\gamma$ -)	Neu reagent	Fluorescent spots under long-wave UV	1
Quinine derivatives	Formic acid vapors	Fluorescent blue spots	3
Sapogenins	Komarowsky reagent	Yellow/pink spots	94
	Paraformaldehyde (0.03% in 85% phosphoric acid)	Variety of spots	88
	Zinc chloride (30% in methanol)	Fluorescent spots after heating (105°C, 1 h) in a moisture-free atmosphere	94
Steroids	Anisaldehyde/sulfuric acid	Variety of colors	95–97
	Antimony (III) chloride (in acetic acid)	Variety of colors	57, 96
	Carr–Price	Variety of colors	1
	Chlorosulfonic acid/acetic acid	Fluorescence under long-wave UV	
	Dragendorff	Variety of spots	78,95
	Formaldehyde (0.03% in phosphoric acid)	Variety of spots	88,89
	Hanes and Isherwood	Variety of spots (only for 3-hydroxy- $\Delta^5$ -steroids)	96
	Liebermann–Burchard	Fluorescence under long-wave UV	1
	Perchloric acid (20%)	Fluorescent spots (long-wave UV) after heating (150°C, 10 min)	1, 44
	Phosphomolybdic acid	Blue color	96
	Phosphoric acid (50%)	Fluorescent spots after heating (120°C) (limit 0.005 $\gamma$ )	95,96,98
	Phosphotungstic acid (10% in ethanol)	Variety of spots	99
	Stannic chloride (5%) in equal volumes of chloroform/acetic acid (1:1)	Variety of spots after heating (100°C, 5 min)	1, 100
	<i>p</i> -Toluenesulfonic acid (20% in chloroform)	Variety of spots	1
	Trichloroacetic acid (50% aqueous)	Fluorescent spots under long-wave UV	50
	Zimmerman	Variety of colors	96
		Variety of colors	95,96
		Variety of spots	99
Sterols	Antimony (III) chloride (50% in acetic acid)		
	Bismuth (III) chloride	Fluorescence under long-wave UV	1
	Chlorosulfonic acid/acetic acid	Fluorescence under long-wave UV	1
	Liebermann–Burchard	Fluorescence under long-wave UV	1

### Spray Reagents in Thin-Layer Chromatography (continued)

Family/ Functional Group	Test	Result	Reference
Sugars	1,2-Naphthoquinone-4-sulfonic acid/perchloric acid	Pink spots that change to blue upon prolonged heating (cholesterol limit 0.03%)	65,101
	Phosphoric acid (50%)	Fluorescent spots after heating (120°C, 15 min)	98,102
	Phosphotungstic acid (10% in ethanol)	Variety of spots	99
	Stannic chloride (5%) in equal volumes of chloroform/acetic acid	Variety of spots after heating (100°C, 5 min)	1
	Sulfuric acid	Variety of spots	102
	<i>o</i> -Aminodiphenyl (0.3%)/orthophosphoric acid (5%)	Brown spots after heating	103
	Aniline/phosphoric acid	Variety of colors	104
	Anisaldehyde/sulfuric acid	Variety of colors	1, 78
	Anthrone test	Yellow spots	105
	Benzidine/trichloroacetic acid	Red–brown/dark spots	106
	Carbazole/sulfuric acid	Violet spots on blue background	103
	Lewis–Smith	Brown spots	107
	Naphthoquinone/perchloric acid	Pink–brown spots (glucose, mannose, lactose, sucrose)	65
	Naphthoresorcinol (0.2% in ethanol)/phosphoric acid (10:1)	Variety of spots after heating (100°C, 5–10 min)	1
	Naphthoresorcinol (0.1%)/sulfuric acid (10%)	Variety of spots after heating (100°C, 5–10 min)	1
	Orcinol reagent	Variety of spots	1
	Permanganate, potassium (0.5% in 1 <i>N</i> sodium hydroxide)	Variety of spots after heating (100°C)	108
	Phenol (3%)/sulfuric acid (5% in ethanol)	Brown spots after heating (100°C, 10 min)	103
	Silver nitrate (0.2% in methanol)/ammonia (saturated)/sodium methoxide (2% in methanol)	Variety of spots after heating (110°C, 10 min)	1
	Silver nitrate/sodium hydroxide	Variety of spots	1
	Sulfuric acid	Variety of spots	108
	Thymol (0.5%) in sulfuric acid (5%)	Pink spots after heating (120°C, 20 min)	103
Sugars, deoxy	Metaperiodate/ <i>p</i> -nitroaniline	Fluorescent (long-wave UV) yellow spots	109
Sugars, ketoses	Anthrone	Bright purple (pentoses); orange–yellow (heptoses); blue fluorescence (aldoses)	110
	Dimedone (0.3%)/phosphoric acid (10% in ethanol)	Dark–gray spots (white light); dark pink fluorescing spots (UV) after heating (110°C, 15 min)	1,111
Sugars, reducing	4-Aminohippuric acid	Fluorescence under long-wave UV	112
	Aniline/diphenylamine/phosphoric acid	Variety of colors	113–115
	Aniline hydrogen phthalate	Variety of colors (limit 1 µg)	116
	<i>p</i> -Anisidine phthalate	Variety of colors	1
	3,5-Dinitrosalicylic acid (0.5% in 4% sodium hydroxide)	Brown spots (sensitivity 1 µg)	3
Sulfides	Ceric ammonium nitrate (in 2 <i>M</i> HNO <sub>3</sub> )	Colorless spots (limit < 100 µg/spot)	117
	Chloranil (1%) in benzene	Yellow–brown spots	119
	2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (2%) in benzene	Purple–blue spots changing to orange upon ammonia exposure	119
	Gibbs	Yellow–brown spots changing to blue–orange upon exposure to ammonia	119

### Spray Reagents in Thin-Layer Chromatography (continued)

Family/ Functional Group	Test	Result	Reference
	Iodine vapors	Brown spots	118
	Tetracyanoethylene (2%) in benzene	Orange spots	119
	N,2,6-Trichloro <i>p</i> -benzoquinoneimine (2%) in ethanol	Brown spots	119
Sulfilimines	Potassium permanganate	Colorless spots	120
Sulfilimines, <i>p</i> -nitrobenzene-sulfonyl	Tin chloride/4- <i>N,N</i> -dimethylaminobenzaldehyde	Yellow spots	121
Sulfites	Malachite green oxalate	White spots on blue background	4
Sulfonamides	Chlorine/pyrazolinone/cyanide	Red spots changing to blue	32
	Diazotization and coupling	Variety of spots (limit 0.25 γ)	122,123
	Ehrlich	Variety of colors	124
	Chloranil (1%) in benzene	Pink turning to violet or green after heating	119
	2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (2%) in benzene	Lilac-violet turning to yellow-green upon ammonia exposure	119
	Gibbs	Violet turning to tan upon exposure to ammonia and heat	119
Sulfones	Iodine vapors	Brown spots	118
	Tetracyanoethylene (2%) in benzene	Pink to yellow upon exposure to ammonia and heat	119
Sulfonic acids	Pinacryptol yellow (0.1%)	Yellow-orange spots under long-wave UV	124
	Silver nitrate/fluorescein	Yellow spots under long-wave UV	125, 126
Sulfoxides	Acetyl bromide	Yellow-orange spots	127
	Ceric ammonium nitrate (40%) in 2 <i>M</i> nitric acid	Brown spots after heating (especially good for α-polychlorosulfoxides); limit 80 μg/spot	117
	Chloranil (1%) in benzene	Yellow-blue spots	119
	2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (2%) in benzene	Orange-crimson spots	119
	Dragendorff	Orange-brown-red spots (limit 30–150 γ)	128
	Gibbs	Yellow turning to brown upon ammonia exposure	168
	Iodide (sodium)/starch	Brown spots (limits 0.01 μmol/20 μl of solution)	129
	Iodine vapors	Brown spots	118,130
	Tetracyanoethylene (2%) in benzene	Yellow or crimson turning to white or tan upon exposure to ammonia	119
	<i>N</i> ,2,6-Trichloro- <i>p</i> -benzoquinoneimine (2%) in ethanol	Yellow spots	119
Terpenes	Anisaldehyde/sulfuric acid	Variety of colors	1
	Antimony (V) chloride	Variety of colors	1
	Carr-rice	Variety of colors	1
	Diphenylpicrylhydrazyl in chloroform	Yellow spots on purple background after heating (110°C) (limit 1γ/0.5 cm diameter)	131
	Phenol (50% in carbon tetrachloride)	Variety of spots upon exposure to bromine vapors	3
	Vanillin (1% in 50% H <sub>3</sub> PO <sub>4</sub> )	Variety of spots after heating (120°C, 20 min)	4
Tetracyclines	Ammonium hydroxide	Yellow fluorescence under long-wave UV	132
Thioacids	Silver nitrate/ammonium hydroxide/sodium chloride	Yellow-brown spots	1
Thiobarbiturates	Cupric sulfate (0.5%)/diethylamine (3% in methanol)	Green spots (limit 15γ)	3,133
Thiolactones	Nitroprusside (sodium), basic	Red spots	62

### Spray Reagents in Thin-Layer Chromatography (continued)

Family/ Functional Group	Test	Result	Reference
Thiols (mercaptans)	Ceric ammonium nitrate (in 2 <i>M</i> nitric acid)	Colorless spots on yellow background (limit <100 µg/spot)	117
	Iodine (1.3% in ethanol)/ethanol	White spots in brown iodine background	3
Thiophenes Thiophosphates, esters	Nitroprusside (sodium) (3%)	Red spots	134
	Isatin (0.4% in conc. sulfuric acid)	Variety of colors	135
	Ferric chloride/sulfosalicylic acid	White spots on violet background	136
	Palladium (II) chloride (0.5% in acidified water)	Variety of spots	1, 136
Unsaturated compounds	Periodic acid (10% in 70% perchloric acid)	Variety of spots	3
	Fluorescein (0.1% in ethanol)/bromine	Yellow spots on a pink background upon exposure to bromine vapors	1
	Osmium tetroxide vapors	Brown/black spots	3,95
Ureas	<i>p</i> - <i>N,N</i> -Dimethylaminobenzaldehyde (1% in ethanol)	Characteristic spots after exposure to hydrochloric acid	4
Vitamin A	Antimony (V) chloride	Variety of colors	1
	Carr–Price	Variety of colors	1
	Sulfuric (50% in methanol) followed by heating	Blue spots that turn brown	1
Vitamin B1	Dipicrylamine	Characteristic spots	3
Vitamin B6	Thiochrome	Variety of spots under long-wave UV	137
	<i>N</i> ,2,6-Trichloro- <i>p</i> -benzoquinoneimine (0.1% in ethanol)	Blue spots after exposure to ammonia	3
Vitamin B6, acetal	2,6-Dibromo- <i>p</i> -benzoquinone-4-chlorimine (0.4% in methanol)	Characteristic spots	138
Vitamin C	Cacotheline (2% aqueous)	Purple spot after heating (100°C)	3
	Iodine (0.005%) in starch (0.4%)	White spot on blue background	3
	Methoxynitroaniline/sodium nitrite	Blue spots on orange background	3
Vitamin D	Animony (V) chloride	Variety of colors	139
	Carr–Price	Variety of colors	1
	Trichloroacetic (1% in chloroform)	Variety of spots after heating (120°C, 5 min)	1
Vitamin E	2',7'-Dichlorofluorescein (0.01% in ethanol)	Spots under long-wave UV light	1
	$\alpha,\alpha'$ -Dipyridyl (0.5%)/ferric chloride (0.5% in ethanol)	Variety of colors	1

## PROTOCOL FOR REAGENT PREPARATION

The following section gives a summary for the preparation of the major spray reagents listed in the previous section (Spray Reagents in Thin-Layer Chromatography). Refer to the original literature for any reagents not listed here.<sup>1-4</sup>

## REFERENCES

1. Krebs, K.G., Heusser, D., and Wimmer, H., *Thin Layer Chromatography, A Laboratory Handbook*, E. Stahl, Ed., Springer-Verlag, Berlin, 1969.
2. Bobbitt, J.B., *Thin Layer Chromatography*, Reinhold, New York, 1963.
3. Touchstone, J.C. and Dobbins, M.F., *Practice of Thin Layer Chromatography*, John Wiley & Sons, New York, 1983.
4. Randerath, K., *Thin-Layer Chromatography*, 2nd ed., Academic Press, New York, 1968.

**Acetic anhydride-sulfuric acid** See *Liebermann-Burchard*.

**Alizarin** A saturated solution of alizarin in ethanol is sprayed on the moist plate, which is then placed in a chamber containing 25% ammonium hydroxide solution to yield a variety of colors.

**Aluminum chloride** A 1% aluminum chloride solution in ethanol is sprayed on the plate, which is then observed under long-wave UV light.

**4-Aminoantipyrine-potassium ferricyanide** See *Emerson*.

**4-Aminobiphenyl-phosphoric acid** See *Lewis-Smith*.

**4-Aminohippuric acid** A 0.3% 4-aminohippuric acid solution in ethanol is sprayed on the plate, which is then heated at 140°C (8 min) and observed under long-wave UV light.

**Ammonium hydroxide** The chromatogram is placed in a chamber containing 25% ammonium hydroxide, dried, and then observed under long-wave UV light.

**Aniline-diphenylamine-phosphoric acid** An aniline (1 g)/diphenylamine (1 g)/phosphoric acid (5 ml) solution in acetone (50 ml) is sprayed on the plate, which is then heated at 85°C (10 min), yielding a variety of colors.

**Aniline-phosphoric acid** A 20% aniline solution in *n*-butanol, saturated with an aqueous (2 *N*) ortho-phosphoric acid solution, is sprayed on the plate, which is then heated at 105°C (10 min), yielding a variety of colors.

**Aniline phthalate** An aniline (1 g)/*o*-phthalic acid (1.5 g) in *n*-butanol (100 ml) (saturated with water) is sprayed on the plate, which is then heated at 105°C (10 min), yielding a variety of colors.

**Anisaldehyde-sulfuric acid** A 1% anisaldehyde solution in acetic acid (acidified by concentrated sulfuric acid) is sprayed on the plate, which is then heated at 105°C to yield a variety of colors.

***p*-Anisidine phthalate** A 0.1 *M* solution of *p*-anisidine and phthalic acid in ethanol is sprayed on the plate, which is then heated at 100°C (10 min) to yield a variety of colors.

**Anthrone** A 1% anthrone solution in 60% aqueous ethanol solution acidified with 10 ml of 60% phosphoric acid is sprayed on the plate, which is then heated at 110°C (5 min) to yield yellow spots.

**Antimony (III) chloride** See *Carr-Price*.

**Antimony (III) chloride-acetic acid** A 20% antimony (III) chloride solution in 75% chloroform-acetic acid solution is sprayed on the plate, which upon heating at 100°C (5 min) yields a variety of colors.

**Antimony (V) chloride** A 20% antimony (V) chloride solution in chloroform or carbon tetrachloride is sprayed on the plate yielding a variety of colors upon heating.

**Benedict reagent** A solution that is 0.1 *M* in cupric sulfate, 1.0 *M* in sodium citrate, and 1.0 *M* in sodium carbonate is sprayed on the plate, which is then observed under long-wave UV light.

**Benzidine diazotized** A 0.5% benzidine solution in 0.005% hydrochloric acid is mixed with an equal volume of 10% sodium nitrite solution in water; the mixture is sprayed on the plate to yield a variety of colors.



- Benzidine-trichloroacetic acid** A 0.5% benzidine in (1:1:8) acetic acid/trichloroacetic acid/ethanol is sprayed on the plate to yield red–brown spots upon heating (110°C) or exposure to unfiltered UV light (15 min).
- Bismuth (III) chloride** A 33% ethanol solution of bismuth (III) chloride is sprayed on the plate, which upon heating (110°C) yields fluorescent spots under long-wave UV light.
- Carbazole-sulfuric acid** A 0.5% carbazole in ethanol/sulfuric acid (95:5) is sprayed on the plate, which yields violet spots (on blue background) after heating at 120°C (10 min).
- Carr–Price** A 25% antimony (III) chloride solution in chloroform or carbon tetrachloride is sprayed on the plate, which is heated at 100°C (10 min) to yield a variety of colors.
- Ceric ammonium sulfate** A 1% solution of ceric ammonium sulfate in strong acids (phosphoric, nitric) is sprayed on the plate to yield yellow/green spots on a red background, after heating at 105°C (10 min).
- Chloramine-T** A 10% chloramine-T solution is sprayed on the plate, followed by 1 *N* hydrochloric acid. The chromatogram is dried and exposed to 25% ammonium hydroxide and warmed.
- Chlorine-pyrazolinone-cyanide** An equal volume mixture of 0.2 *M* 1-phenyl-3-methyl-2-pyrazolin-5-one solution (in pyridine) and 1 *M* aqueous potassium cyanide solution is sprayed on the plate that has been previously exposed to chlorine vapors. The resulting red spots turn blue after a few minutes.
- Chlorosulfonic acid-acetic acid** A 35% chlorosulfonic acid solution in acetic acid is sprayed on the plate, which is then heated at 130°C (5 min) to produce fluorescence under long-wave UV.
- Cinnamaldehyde-hydrochloric acid** A 5% cinnamaldehyde solution in ethanol (acidified with hydrochloric acid) is sprayed on the plate, which is then placed in a hydrochloric acid chamber to yield red spots.
- Cobalt (II) thiocyanate** An ammonium thiocyanate (15%)/cobalt (II) chloride (5%) solution in water is sprayed on the plate, yielding blue spots.
- Cupric sulfate-quinine-pyridine** A solution that is 0.4% in cupric sulfate, 0.04% in quinine hydrochloride, and 4% in pyridine in water is sprayed on the plate followed by a 0.5% aqueous potassium permanganate solution. A variety of colors (white, yellow, violet) are detected on the chromatogram.
- $\alpha$ -Cyclodextrin** A 30%  $\alpha$ -cyclodextrin solution in ethanol is sprayed on the plate, which is further developed in an iodine chamber.
- Diazonium** See *Fast Blue B Salt*.
- Diazotization and coupling** A 1% sodium nitrite solution (in 1 *M* hydrochloric acid) is sprayed on the plate, followed by a 0.2%  $\alpha$ -naphthol solution in 1 *M* potassium hydroxide and drying.
- 4-*N,N*-Dimethylaminobenzaldehyde-sulfuric acid** A 0.125% solution of 4-*N,N*-dimethylaminobenzaldehyde in 65% sulfuric acid mixed with 5% ferric chloride (0.05 ml per 100 ml solution) is sprayed on the plate, giving a variety of spots.
- 4-*N,N*-Dimethylaminocinnamaldehyde** A 0.2% solution of 4-*N,N*-dimethylaminocinnamaldehyde in 6 *N* HCl/ethanol (1:4) is sprayed on the plate, which is then heated at 105°C (5 min), revealing a variety of colored spots. Vapors of aqua regia tend to intensify the spots.
- 2,4-Dinitrofluorobenzene** A 1% sodium bicarbonate solution in 0.025 *M* sodium hydroxide is sprayed on the plate followed by a 2,4-dinitrofluorobenzene (10%) solution in methanol. Heating the plate in the dark (40°C, 1 h) and further spraying it with diethyl ether yields a variety of spots.
- 2,4-Dinitrophenylhydrazine** A 0.4% solution of 2,4-dinitrophenylhydrazine in 2 *N* hydrochloric acid is sprayed on the plate followed by a 0.2% solution of potassium ferricyanide in 2 *N* hydrochloric acid yielding orange/yellow spots.
- Dragendorff** A 1.7% aqueous solution of basic bismuth nitrate in weak acids (tartaric, acetic) mixed with an aqueous potassium iodide or barium chloride solution is sprayed on the plate to yield a variety of spots.
- Ehrlich** A 1% 4-*N,N*-dimethylaminobenzaldehyde solution in ethanol is sprayed on the plate, which is dried and then placed in a hydrochloric acid chamber to yield various spots.
- Emerson** A 2% 4-aminoantipyrine solution in ethanol is sprayed on the plate, followed by an 8% aqueous potassium ferricyanide solution. The chromatogram is then placed in a chamber containing 25% ammonium hydroxide.

- EP** A 0.3% solution of 4-*N,N*-dimethylaminobenzaldehyde in acetic acid/phosphoric acid/water (10:1:4) is sprayed on the plate to yield a variety of spots.
- Fast Blue B salt (diazonium)** A 0.5% aqueous solution of Fast Blue B Salt is sprayed on the plate followed by a 0.1 *M* sodium hydroxide.
- Ferric chloride-perchloric acid** A solution made of 5 ml of 5% aqueous ferric chloride, 45 ml of 20% perchloric acid, and 50 ml of 50% nitric acid is sprayed on the plate to yield a variety of spots.
- Ferric chloride-sulfosalicylic acids** The plate is first exposed to a bromine atmosphere and then sprayed with a 0.1% ethanolic solution of ferric chloride. After air drying (15 min), the chromatogram is sprayed with a 1% ethanolic solution of sulfosalicylic acid to yield a variety of spots.
- Ferrocyanide-hydrogen peroxide** Ammonium chloride (0.5 g) is added to a 0.1% potassium ferrocyanide solution in 0.2% hydrochloric acid, and the resulting solution is sprayed on the plate, which is then dried (100°C). The chromatogram is further sprayed with 30% hydrogen peroxide, heated (150°C, 30 min), and sprayed with 10% potassium carbonate to yield yellow/red spots.
- Ferrous thiocyanate** A 2:3 mixture of a 4% aqueous ferrous sulfate and 1.3% acetone solution of ammonium thiocyanate is sprayed on the plate yielding red–brown spots.
- Fluorescein-hydrogen peroxide** A 0.1% fluorescein solution in 50% aqueous ethanol is sprayed on the plate followed by a 15% hydrogen peroxide in glacial acetic acid and heated (90°C, 20 min), yielding nonfluorescent spots.
- Folin** A 0.02% sodium 1,2-naphthoquinone-4-sulfonate in 5% sodium carbonate is sprayed on the plate, which is then dried to yield a variety of colors.
- Folin–Denis** A tungstomolybdophosphoric acid solution is sprayed on the plate, which is then exposed to ammonia vapors.
- Gibbs** A 0.4% methanolic solution of 2,6-dibromoquinonechloroimide is sprayed on the plate followed by a 10% aqueous sodium carbonate, yielding a variety of spots.
- Glucose-phosphoric acid** A 2% glucose solution in phosphoric acid/water/ethanol/*n*-butanol (1:4:3:3) is sprayed on the plate followed by heating (115°C, 10 min) to yield a variety of spots.
- Hydroxylamine-ferric chloride** A 1:2 mixture of a 10% hydroxylammonium chloride/10% potassium hydroxide in aqueous ethanol is sprayed on the plate followed by drying. The chromatogram is then sprayed with an ether solution of ferric chloride in hydrochloric acid to yield a variety of spots.
- Iodide (potassium) starch** A 1% potassium iodide solution in 80% aqueous acetic acid is sprayed on the plate followed by a 1% aqueous starch solution. A pinch of zinc dust is recommended as an addition to the potassium iodide solution.
- Iodide (sodium) starch** A solution made by mixing a 5% starch/0.5% sodium iodide solution with an equal volume of concentrated hydrochloric acid is sprayed on the plate, which is then exposed to dry sodium hydroxide (desiccator) and evacuated (30 to 60 min) to yield brown spots.
- Isatin-zinc acetate** An isatin (1%)/zinc acetate (1.5%) solution in isopropanol acidified with acetic acid is sprayed on the plate, which is then heated to yield a variety of spots.
- Kalignost** A 1% solution of sodium tetraphenylborate in aqueous butanone is sprayed on the plate, followed by a 0.015% methanolic solution of fischtin or quercetin to yield orange–red spots that fluoresce under long-wave UV.
- König** A 2% *p*-aminobenzoic acid in ethanolic hydrochloric acid (0.6 *M*) is sprayed on the plate that has been exposed (1 h) to vapors of cyanogen bromide.
- Komarowski** A 2% methanolic solution of *p*-hydroxybenzaldehyde that is 5% in sulfuric acid is sprayed on the plate, which is then heated (105°C, 3 min) to yield yellow or pink spots.
- Lewis–Smith** *o*-Aminobiphenyl (0.3 g dissolved in 100 ml of a 19:1 ethanol/phosphoric acid mixture) is sprayed on the plate, which is then heated at 110°C (15 min).
- Liebermann–Burchard** A freshly prepared mixture of 5 ml of acetic anhydride/5 ml of concentrated sulfuric acid in 50 ml of cold absolute ethanol is sprayed on the plate, which is heated at 100°C (10 min) and observed under long-wave UV light.
- Malachite green oxalate** A 1% ethanolic potassium hydroxide solution is sprayed, and the plate is heated (150°C, 5 min) and further sprayed with a buffered (pH = 7) water/acetone solution of malachite green oxalate to yield white spots on a blue background.
- Metaperiodate (sodium)-*p*-nitroaniline** A 35% saturated solution of sodium metaperiodate is sprayed on the plate, which is left to dry (10 min). The chromatogram is then sprayed with a 0.2%

*p*-nitroaniline solution in ethanol/hydrochloric acid (4:1) to yield fluorescing (long-wave UV) yellow spots.

**Methoxynitroaniline-sodium nitrite** A 0.02 *M* 4-methoxy-2-nitroaniline solution in 50% aqueous acetic acid/5 *N* sulfuric acid is sprayed on the plate, which is dried and resprayed with 0.2% sodium nitrite to yield blue spots on an orange background.

**Millon reagent** A solution of mercury (5 g) in fuming nitric acid (10 ml) diluted with water (10 ml) is sprayed on the plate to yield yellow/orange spots that are intensified by heat (100°C).

**1,2-Naphthoquinone-4-sulfonic acid/perchloric acid** A 0.1% 1,2-naphthoquinone-4-sulfonic acid solution in ethanol/perchloric acid/40% formaldehyde/water (20:10:1:9) is sprayed on the plate, which is then heated (70°C) to yield pink spots that turn to blue on prolonged heating.

**Neu reagent** A 1% methanolic solution of the  $\beta$ -aminoethylester of diphenylboric acid is sprayed on the plate to yield fluorescent spots under long-wave UV light.

**Ninhydrin** A ninhydrin solution (0.3% in acidified 1-butanol or 0.2% in ethanol) is sprayed on the plate, which is then heated (110°C). The resulting spots are stabilized by spraying with a solution made of 1 ml of saturated aqueous cupric nitrate, 0.2 ml of 10% nitric acid, and 100 ml of 95% ethanol, to yield red spots when exposed to ammonium hydroxide (25%).

***p*-Nitroaniline, diazotized** A solution made by mixing 0.1% aqueous *p*-nitroaniline/0.2% aqueous sodium nitrite/10% aqueous potassium carbonate (1:1:2) is sprayed on the plate to yield colored spots.

***p*-Nitroaniline, diazotized (buffered)** A solution of 0.5% *p*-nitroaniline (in 2 *N* hydrochloric acid), 5% aqueous sodium nitrite, and 20% aqueous sodium acetate (10:1:30) is sprayed on the plate to yield a variety of colored spots.

**Nitroprusside (sodium)** A solution made by mixing sodium nitroprusside (1.5 g), 2 *N* hydrochloric acid (5 ml), methanol (95 ml), and 25% ammonium hydroxide (10 ml) is sprayed on the plate to yield a variety of colors.

**Nitroprusside (sodium), basic** A 2% sodium nitroprusside solution in 75% ethanol is sprayed on the plate, which has already been treated with 1 *N* sodium hydroxide to yield red spots.

**Orcinol** A mixture consisting of 0.6% ethanolic orcinol and 1% ferric chloride in dilute sulfuric acid is sprayed on the plate, which is further heated (100°C, 10 min) to yield characteristic spots.

**Prochazka** A 10% formaldehyde solution in 5% hydrochloric acid solution in ethanol is sprayed on the plate, which is then heated to yield fluorescent spots (yellow/orange/green) under long-wave UV.

**Quercetin-sodium tetraphenylborate** A mixture of quercetin (0.015% in methanol) and sodium tetraphenyl-borate (1% in *n*-butanol saturated with water) is sprayed on the plate to yield orange/red spots.

**Quinaldine** A 1 to 1.5% solution of 3,5-diaminobenzoic acid dihydrochloride in 30% phosphoric acid is sprayed on the plate, which is then heated (100°C, 15 min) to yield fluorescent (green/yellow) spots under long-wave UV or (in case of high concentrations) brown spots in daylight.

**Sakaguchi** A 0.1% acetone solution of 8-hydroxyquinoline is sprayed on the plate followed by a 0.2% 0.5 *N* sodium hydroxide solution to yield orange/red spots.

**Salkowski** A 0.01 *M* aqueous ferric chloride/35% perchloric acid solution is sprayed on the plate, which is then heated (60°C, 5 min) to yield a variety of colors intensified when exposed to aqua regia.

**Schweppe** A mixture of 2% aqueous glucose/2% ethanolic aniline in *n*-butanol is sprayed on the plate, which is heated (125°C, 5 min) to yield a variety of spots.

**Silver nitrate-ammonium hydroxide-sodium chloride** A mixture of silver nitrate (0.05 *M*)/ammonium hydroxide (5%) is sprayed on the plate, followed by drying and further spraying with 10% aqueous sodium chloride to yield yellow/brown spots.

**Silver nitrate-fluorescein** A mixture of silver nitrate (2%)/sodium-fluorescein (0.2%) in 80% ethanol is sprayed on the plate to yield yellow spots on a pink background.

**Silver nitrate-formaldehyde** The plate is consecutively sprayed with 0.05 *M* ethanolic silver nitrate, 35% aqueous formaldehyde, 2 *M* potassium hydroxide, and, finally, a solution made of equal volumes of hydrogen peroxide (30%) and nitric acid (65%). Each spraying is preceded by a 30-min drying, and at the end, the plate is kept in the dark for 12 h before exposure to sunlight to yield dark gray spots.

**Silver nitrate-hydrogen peroxide** A 0.05% silver nitrate solution in water/cellosolve/acetone (1:10:190) (to which a drop of 30% hydrogen peroxide has been added) is sprayed on the plate, which is then treated under unfiltered UV to yield dark spots.

**Silver nitrate-sodium hydroxide** A saturated silver nitrate solution is sprayed on the plate followed by a 0.5 *M* aqueous/methanol solution. Subsequent drying (100°C, 2 min) yields a variety of spots.

**Sonnenschein** A 2% ceric sulfate solution in 20% aqueous trichloroacetic acid (that has been acidified with sulfuric acid) is sprayed on the plate. A variety of colors appear upon heating (110°C, 5 min).

**Stahl** See *van Urk*.

**Sulfanilic acid-1-naphthylamine** A mixture of sulfanilic acid/1-naphthylamine in 30% acetic acid is sprayed on the plate to yield a variety (violet/green/blue) of colors.

**Thiochrome** A 0.3 *M* aqueous potassium ferricyanide solution that is 15% in sodium hydroxide is sprayed on the plate, yielding a variety of spots under long-wave UV.

**Tollen's** See *Zaffaroni*.

**Vanillin-potassium hydroxide** A 2% solution of vanillin in *n*-propanol is sprayed on the plate, which is heated (100°C, 10 min) and sprayed again with 1% ethanolic potassium hydroxide. Reheating yields a variety of colors observed under daylight.

**van Urk (Stahl)** A 0.5% solution of 4-*N,N*-dimethylaminobenzaldehyde in concentrated hydrochloric acid/ethanol (1:1) is sprayed on the preheated plate, which is then subjected to aqua regia vapors to yield a variety of colors.

**Zaffaroni (Tollen's)** A mixture of silver nitrate (0.02 *M*)/ammonium hydroxide (5 *M*) is sprayed on the plate, which is then heated (105°C, 10 min) to yield black spots.

**Zwikker** A 1% cobaltous nitrate in absolute ethanol is sprayed on the plate, which is dried (at room temperature) and exposed to a wet chamber containing 25% ammonium hydroxide.

## CHAPTER 4

# Supercritical Fluid Extraction and Chromatography

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## SOME USEFUL FLUIDS FOR SUPERCRITICAL FLUID EXTRACTION AND CHROMATOGRAPHY

The following table lists some useful carrier and modifier fluids for supercritical fluid extraction and chromatography, along with relevant properties.<sup>1-7</sup> The critical properties are needed to determine successful fluid operating ranges. Where possible, experimental values are provided. In some cases, however, values calculated with a group contribution approach are presented.<sup>2</sup> These entries are marked with an asterisk. The dipole moment is provided to assess fluid polarity, although these values can be temperature dependent, especially with the more complex fluids. Occasionally, conformations change with temperature, resulting in a change in dipole moment. Data on ultraviolet cutoff are provided to allow the application of UV-vis monitoring instrumentation. Data are not provided if the only electronic transition is in the very low wavelength range, and the spectrum is largely flat. With respect to the halocarbon fluids, if a commonly used refrigerant designator is available, it is presented with the chemical name. The fluids listed here have been either used or proposed for use in supercritical fluid chromatography or supercritical fluid extraction. Note that some of these fluids (for example, methanol and toluene) will undergo serious chemical degradation under near-critical conditions while in contact with stainless steels and other common materials.<sup>4-6</sup>

## REFERENCES

1. Bruno, T.J. and Svoronos, P.D.N., *Basic Tables for Chemical Analysis*, NBS-TN-1096, Washington, D.C., 1986.
2. Bruno, T.J. and Ely, J.F., *Supercritical Fluid Technology, Reviews in Modern Theory and Applications*, CRC Press, Boca Raton, FL, 1991.
3. Bruno, T.J., *CRC Handbook for the Identification and Analysis of Alternative Refrigerants*, CRC Press, Boca Raton, FL, 1995.
4. Bruno, T.J. and Straty, G.C., Thermophysical property measurement on chemically reactive systems: a case study, *J. Res. Natl. Bur. Stand. (U.S.)*, 91, 135, 1986.
5. Straty, G.C., Ball, M.J., and Bruno, T.J., Experimental determination of the PVT surface for benzene, *J. Chem. Eng. Data*, 32, 163, 1987.
6. Asche, W., Mobile phases for supercritical fluid chromatography, *Chromatographia*, 11, 411, 1978.
7. Goodwin, A.R.H. and Mehl, J.B., Measurement of the dipole moments of seven partially fluorinated hydrocarbons with a radiofrequency reentrant cavity resonator, *Int. J. Thermophysics*, 18, 795-806, 1997.

### Some Useful Fluids for Supercritical Fluid Extraction and Chromatography

Fluid	T <sub>c</sub> (°C)	ρ <sub>c</sub> (g/ml)	P <sub>c</sub> (MPa)	μ (D)	UV cutoff, nm
<b>Inorganic Fluids</b>					
Carbon dioxide	31.413	0.460	7.4	0.0	
Ammonia	132.5	0.235	11.4	1.47	
Nitrous oxide	36.5	0.450	7.3	0.167	
Sulfur dioxide	157.8	0.520	7.9	1.63	
Sulfur hexafluoride	45.6	0.730	3.76	0.0	
Water	374.1	0.40	22.1	1.85	
Xenon	16.6	1.155	5.9		
<b>Hydrocarbon Fluids</b>					
Ethane	32.19	0.203	4.871	0.0	
Propane	96.8	0.220	4.26	0.066*	
<i>n</i> -Butane	152.05	1.225	3.80	0.001*	
<i>n</i> -Pentane	196.6	0.232	3.4	0.055*	
<i>n</i> -Hexane	234.2	0.234	3.0	0.08*	250
Benzene	288.9	0.304	4.9	0.0	325
Toluene	320.8	0.29	4.2	0.084	325
<b>Alcohols, Ethers, and Ketones</b>					
Methanol	239.5	0.272	8.0	1.70	255
Ethanol	240.8	0.275	6.14	1.7	255
Isopropanol	235.3	0.273	4.8	1.66	255
Dimethyl ether	126.9	0.271	5.24	1.3	
Diethyl ether	193.4	0.265	3.651	1.3	225
Acetone	235	0.278	4.7	2.9	350

\* Dipole moments for these *n*-alkanes were calculated with the Hartree-Fock method, using the 6-31G\* basis set, PC-Spartan-Plus, Version 2.0.0, March 1, 2000.

**Some Useful Fluids for Supercritical Fluid Extraction and Chromatography (continued)**

Fluid	T <sub>c</sub> (°C)	ρ <sub>c</sub> (g/ml)	P <sub>c</sub> (MPa)	μ (D)	UV cutoff, nm
<b>Halocarbons</b>					
Fluoromethane, R-41	41.9	0.301	5.6	1.8	285
Difluoromethane, R-32	78.41	0.430	5.83	1.978	240
Trifluoromethane, R-23	25.83	0.526	4.82	1.65	300
Chloromethane, R-40	143.15	0.364	6.7	1.87	240
Chlorodifluoro methane, R-22	96.15	0.521	4.97	1.44	220
Dichlorofluoro methane, R-21	178.5	0.522	5.2	1.24	235
Trichlorofluoro methane, R-11	198	0.554	4.4	0.45	235
Chlorotrifluoro methane, R-13	28.9	0.578	3.9	0.5	220
Dichlorodifluoro methane, R-12	111.5	0.558	4.0	0.51	245
Fluoroethane, R-161	102.16	0.288	4.70	1.94	210
1,1-Difluoroethane, R-152a	113.5	0.365	4.49	2.262	
1,1,1-Trifluoroethane, R-143a	73.1	0.434	3.76	2.32	
1,1,2-Trifluoroethane, R-143	156.75	0.466	4.52	1.68 (35.9°C) 1.75 (136.9°C)	
1,1,1,2-Tetrafluoroethane, R-134a	101.06	0.515	4.06	2.058	
1,1,2,2-Tetrafluoroethane, R-134	118.95	0.542	4.56	0.991 (36°C) 0.250 (140°C)	300
Pentafluoroethane, R-125	68.3	0.572	3.631	1.54	
1,1-Dichlorotetrafluoro ethane, R-114a	145.7	0.582	3.6	0.496 <sup>1</sup>	
1-Chloro-1,1-difluoroethane	137.1	0.435	4.12	2.14	265
1,2-Dichloro tetrafluoroethane	145.7	0.582	3.26	0.668 (35°C) 0.699 (137°C)	240
2-Chloro-1,1,1,2-tetrafluoroethane, R-124	122.5	0.554	3.63	1.469	230
Chloropentafluoro ethane, R-115	79.9	0.596	3.12	0.52	245
1,1,1,2,3,3-Hexafluoropropane, R-236ea	141.1	0.571	3.533	1.129	
1,1,1,2,3,3,3-Heptafluoropropane, R-227ea	102.8	0.580	2.94	1.456	
2-Chloroheptafluoro propane, R-217ba	127.5*	0.592*	3.12*	0.402 <sup>1</sup>	210
Bis(difluoromethyl) ether, E-134	147.6	0.522	4.302	1.739 (36°C) 1.840 (173°C)	

<sup>1</sup>This dipole moment was calculated with the Hartree-Fock method, using the 6-31G\* basis set, PC-Spartan-Plus, Version 2.0.0, March 1, 2000.



## P-ρ-T TABLE FOR CARBON DIOXIDE

The following table provides a numerical listing of the P-ρ-T surface for carbon dioxide in the region of interest for supercritical fluid extraction and chromatography. These data were calculated using an empirical equation of state (the Schmidt–Wagner equation),<sup>1,2</sup> the parameters of which were determined from a fit of experimental P-V-T (pressure-volume-temperature) measurements.<sup>3–8</sup> Note that the pressures are tabulated in bars for convenience. The appropriate SI unit of pressure is the megapascal (1 bar = 0.1 MPa).

### REFERENCES

1. Schmidt, R. and Wagner, W., A new form of the equation of state for pure substances and its application to oxygen, *Fluid Phase Equilibria*, 19, 175, 1985.
2. Ely, J.F., National Bureau of Standards, Boulder, CO (private communication on coefficients for carbon dioxide), 1986.
3. Poling, B.E., Prausnitz, J.M., and O'Connell, J.P., *The Properties of Gases and Liquids*, 5th ed., McGraw-Hill, 2000.
4. Prausnitz, J.M., *Molecular Thermodynamics of Fluid Phase Equilibria*, Prentice Hall, Englewood Cliffs, 1969.
5. Chao, K.C. and Greenkorn, R.A., *The Thermodynamics of Fluids*, Marcel Dekker, New York, 1975.
6. Jacobson, R.T. and Stewart, R.B., Thermodynamic properties of nitrogen including liquid and vapor phases from 63 K to 2000 K with pressures to 10,000 bar, *J. Phys. Chem. Ref. Data*, 2, 757, 1973.
7. Ely, J.F., Proceedings of the 63rd Gas Processors Association Annual Convention, San Antonio, TX, 1984, p. 9.
8. Angus, S., Armstrong, B., and deReuck, K.M., *Carbon Dioxide, International Thermodynamic Tables of the Fluid State*, Pergamon Press, Oxford, 1976.

**P-ρ-T Table for Carbon Dioxide**

Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)
<b>Temperature = 308.15 K</b>					
0.20	5.009	2.40	46.323	4.60	67.661
0.30	7.429	2.50	47.668	4.70	68.282
0.40	9.792	2.60	48.971	4.80	68.878
0.50	12.100	2.70	50.235	4.90	69.450
0.60	14.353	2.80	51.460	5.00	69.998
0.70	16.552	2.90	52.646	5.10	70.523
0.80	18.698	3.00	53.795	5.20	71.027
0.90	20.791	3.10	54.907	5.30	71.509
1.00	22.832	3.20	55.983	5.40	71.970
1.10	24.821	3.30	57.024	5.50	72.410
1.20	26.760	3.40	58.030	5.60	72.831
1.30	28.648	3.50	59.002	5.70	73.233
1.40	30.487	3.60	59.941	5.80	73.617
1.50	32.278	3.70	60.847	5.90	73.983
1.60	34.020	3.80	61.722	6.00	74.332
1.70	35.716	3.90	62.565	6.10	74.665
1.80	37.365	4.00	63.379	6.20	74.981
1.90	38.968	4.10	64.162	6.30	75.282
2.00	40.526	4.20	64.917	6.40	75.569
2.10	42.040	4.30	65.644	6.50	75.841
2.20	43.510	4.40	66.343	6.60	76.100
2.30	44.938	4.50	67.015	6.70	76.345

P-p-T Table for Carbon Dioxide

Density, $\rho$ (mol/l)	Pressure, P (bar)	Density, $\rho$ (mol/l)	Pressure, P (bar)	Density, $\rho$ (mol/l)	Pressure, P (bar)
Temperature = 308.15 K (continued)					
6.80	76.578	12.30	81.957	17.80	128.308
6.90	76.800	12.40	82.065	17.90	130.874
7.00	77.010	12.50	82.180	18.00	133.554
7.10	77.209	12.60	82.301	18.10	136.350
7.20	77.398	12.70	82.430	18.20	139.267
7.30	77.577	12.80	82.567	18.30	142.309
7.40	77.746	12.90	82.713	18.40	145.478
7.50	77.907	13.00	82.868	18.50	148.781
7.60	78.060	13.10	83.033	18.60	152.221
7.70	78.205	13.20	83.210	18.70	155.802
7.80	78.342	13.30	83.399	18.80	159.530
7.90	78.473	13.40	83.601	18.90	163.407
8.00	78.597	13.50	83.817	19.00	167.440
8.10	78.515	13.60	84.047	19.10	171.633
8.20	78.828	13.70	84.294	19.20	175.991
8.30	78.935	13.80	84.558	19.30	180.519
8.40	79.037	13.90	84.841	19.40	185.222
8.50	79.135	14.00	85.143	19.50	190.105
8.60	79.228	14.10	85.466	19.60	195.173
8.70	79.318	14.20	85.811	19.70	200.432
8.80	79.405	14.30	86.179	19.80	205.887
8.90	79.488	14.40	86.573	19.90	211.544
9.00	79.568	14.50	86.993	20.00	217.408
9.10	79.646	14.60	87.441	20.10	223.485
9.20	79.721	14.70	87.919	20.20	229.781
9.30	79.794	14.80	88.427	20.30	236.302
9.40	79.865	14.90	88.969	20.40	243.053
9.50	79.935	15.00	89.545	20.50	250.040
9.60	80.003	15.10	90.158	20.60	257.271
9.70	80.069	15.20	90.808	20.70	264.750
9.80	80.135	15.30	91.499	20.80	272.484
9.90	80.200	15.40	92.231	20.90	280.480
10.00	80.264	15.50	93.007	21.00	288.743
10.10	80.328	15.60	93.829	21.10	297.280
10.20	80.391	15.70	94.700	21.20	306.098
10.30	80.454	15.80	95.620	21.30	315.203
10.40	80.517	15.90	96.592	21.40	324.601
10.50	80.580	16.00	97.619	21.50	334.300
10.60	80.643	16.10	98.703	21.60	344.307
10.70	80.706	16.20	99.845	21.70	354.627
10.80	80.771	16.30	101.049	21.80	365.268
10.90	80.835	16.40	102.317	21.90	376.236
11.00	80.901	16.50	103.652	22.00	387.540
11.10	80.968	16.60	105.055	22.10	399.185
11.20	81.037	16.70	106.530	22.20	411.179
11.30	81.107	16.80	108.079	22.30	423.529
11.40	81.178	16.90	109.706	22.40	436.242
11.50	81.252	17.00	111.412	22.50	449.326
11.60	81.328	17.10	113.201	22.60	462.787
11.70	81.407	17.20	115.076	22.70	476.634
11.80	81.489	17.30	117.040	22.80	490.874
11.90	81.574	17.40	119.096	22.90	505.514
12.00	81.663	17.50	121.428	23.00	520.562
12.10	81.756	17.60	123.498	23.10	536.026
12.20	81.854	17.70	125.850	23.20	551.914

P-ρ-T Table for Carbon Dioxide

Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)
Temperature = 308.15 K (continued)					
23.30	568.233	23.90	675.660	24.50	800.709
23.40	584.991	24.00	695.227	24.60	823.398
23.50	602.197	24.10	715.292	24.70	846.639
23.60	619.859	24.20	735.864	24.80	870.441
23.70	637.984	24.30	756.952	24.90	894.816
23.80	656.582	24.40	778.564	25.00	919.772
Temperature = 313.15 K					
0.20	5.095	4.70	71.463	9.20	87.080
0.30	7.559	4.80	72.148	9.30	87.241
0.40	9.968	4.90	72.180	9.40	87.401
0.50	12.323	5.00	73.449	9.50	87.558
0.60	14.625	5.10	74.006	9.60	87.714
0.70	16.874	5.20	74.661	9.70	87.869
0.80	19.070	5.30	75.235	9.80	88.023
0.90	21.215	5.40	75.788	9.90	88.176
1.00	23.309	5.50	76.322	10.00	88.329
1.10	25.352	5.60	76.836	10.10	88.481
1.20	27.346	5.70	77.332	10.20	88.634
1.30	29.291	5.80	77.810	10.30	88.787
1.40	31.188	5.90	78.271	10.40	88.940
1.50	33.038	6.00	78.714	10.50	89.095
1.60	34.840	6.10	79.142	10.60	89.250
1.70	36.597	6.20	79.553	10.70	89.407
1.80	38.308	6.30	79.950	10.80	89.566
1.90	39.975	6.40	80.331	10.90	89.727
2.00	41.598	6.50	80.699	11.00	89.890
2.10	43.177	6.60	81.053	11.10	90.056
2.20	44.714	6.70	81.395	11.20	90.224
2.30	46.209	6.80	81.723	11.30	90.397
2.40	47.664	6.90	82.040	11.40	90.572
2.50	49.078	7.00	82.345	11.50	90.753
2.60	50.453	7.10	82.640	11.60	90.937
2.70	51.788	7.20	82.923	11.70	91.127
2.80	53.086	7.30	83.197	11.80	91.322
2.90	54.346	7.40	83.462	11.90	91.523
3.00	55.570	7.50	83.717	12.00	91.730
3.10	56.758	7.60	83.964	12.10	91.944
3.20	57.911	7.70	84.202	12.20	92.166
3.30	59.029	7.80	84.433	12.30	92.396
3.40	60.114	7.90	84.657	12.40	92.635
3.50	61.165	8.00	84.874	12.50	92.883
3.60	62.185	8.10	85.084	12.60	93.141
3.70	63.172	8.20	85.289	12.70	93.410
3.80	64.129	8.30	85.487	12.80	93.691
3.90	65.056	8.40	85.681	12.90	93.984
4.00	65.953	8.50	85.869	13.00	94.290
4.10	66.821	8.60	86.053	13.10	94.610
4.20	67.661	8.70	86.233	13.20	94.945
4.30	68.474	8.80	86.409	13.30	95.296
4.40	69.260	8.90	86.581	13.40	95.664
4.50	70.019	9.00	86.750	13.50	96.049
4.60	70.754	9.10	86.917	13.60	96.453

P-ρ-T Table for Carbon Dioxide

Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)
Temperature = 313.15 K (continued)					
13.70	96.878	17.50	143.517	21.30	353.863
13.80	97.323	17.60	146.104	21.40	363.790
13.90	97.791	17.70	148.798	21.50	374.021
14.00	98.283	17.80	151.603	21.60	384.564
14.10	98.799	17.90	154.522	21.70	395.426
14.20	99.341	18.00	157.558	21.80	406.613
14.30	99.911	18.10	160.717	21.90	418.132
14.40	100.510	18.20	164.001	22.00	429.990
14.50	101.139	18.30	167.414	22.10	442.195
14.60	101.800	18.40	170.962	22.20	454.753
14.70	102.495	18.50	174.647	22.30	467.672
14.80	103.224	18.60	178.474	22.40	480.958
14.90	103.991	18.70	182.449	22.50	494.620
15.00	104.796	18.80	186.574	22.60	508.664
15.10	105.640	18.90	190.855	22.70	523.099
15.20	106.527	19.00	195.297	22.80	537.931
15.30	107.458	19.10	199.904	22.90	553.168
15.40	108.435	19.20	204.681	23.00	568.818
15.50	109.459	19.30	209.633	23.10	601.389
15.60	110.533	19.40	214.766	23.20	601.389
15.70	111.659	19.50	220.084	23.30	618.325
15.80	112.839	19.60	225.592	23.40	635.705
15.90	114.075	19.70	231.296	23.50	653.539
16.00	115.369	19.80	237.201	23.60	671.833
16.10	116.725	19.90	243.314	23.70	690.597
16.20	118.143	20.00	249.638	23.80	709.839
16.30	119.627	20.10	256.181	23.90	729.567
16.40	121.179	20.20	262.947	24.00	749.790
16.50	122.801	20.30	269.943	24.10	770.517
16.60	124.496	20.40	277.175	24.20	791.756
16.70	126.268	20.50	284.648	24.30	813.518
16.80	128.118	20.60	292.368	24.40	835.810
16.90	130.049	20.70	300.342	24.50	858.643
17.00	132.065	20.80	308.576	24.60	882.025
17.10	134.168	20.90	317.076	24.70	905.967
17.20	136.362	21.00	325.848	24.80	930.477
17.30	138.649	21.10	334.899	24.90	955.567
17.40	141.033	21.20	344.235	25.00	981.245
Temperature = 318.15 K					
0.20	5.180	1.50	33.793	2.90	56.028
0.30	7.689	1.60	35.655	3.00	57.325
0.40	10.144	1.70	37.472	3.10	58.588
0.50	12.546	1.80	39.245	3.20	59.816
0.60	14.896	1.90	40.974	3.30	61.110
0.70	17.194	2.10	44.305	3.40	62.172
0.80	19.440	2.20	45.908	3.50	63.301
0.90	21.637	2.30	47.470	3.60	64.399
1.00	23.783	2.40	48.992	3.70	65.466
1.10	25.881	2.50	50.475	3.80	66.503
1.20	27.930	2.60	51.919	3.90	67.511
1.30	29.931	2.70	53.326	4.00	68.490
1.40	31.885	2.80	54.695	4.10	69.441

P-ρ-T Table for Carbon Dioxide

Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)
Temperature = 318.15 K (continued)					
4.20	70.364	9.80	95.886	15.20	122.559
4.30	71.261	9.90	96.435	15.30	123.725
4.40	72.131	10.00	96.385	15.40	124.942
4.50	72.976	10.10	96.635	15.50	126.209
4.60	73.797	10.20	96.886	15.60	127.530
4.70	74.593	10.30	97.138	15.70	128.907
4.80	75.365	10.40	97.392	15.80	130.341
4.90	76.115	10.50	97.648	15.90	131.836
5.00	76.842	10.60	97.906	16.00	133.392
5.10	77.547	10.70	98.167	16.10	135.014
5.20	78.231	10.80	98.431	16.20	136.702
5.30	78.895	10.90	98.669	16.30	138.461
5.50	80.163	11.00	98.970	16.40	140.291
5.60	80.769	11.10	99.246	16.50	142.196
5.70	81.356	11.20	99.527	16.60	144.178
5.80	81.926	11.30	99.813	16.70	146.241
5.90	82.479	11.40	100.104	16.80	148.387
6.00	83.015	11.50	100.402	16.90	150.618
6.10	83.535	11.60	100.707	17.00	152.938
6.20	84.039	11.70	101.018	17.10	155.351
6.30	84.529	11.80	101.338	17.20	157.858
6.40	85.004	11.90	101.666	17.30	160.463
6.50	85.466	12.00	102.003	17.40	163.170
6.60	85.914	12.10	102.349	17.50	165.982
6.70	86.349	12.20	102.705	17.60	168.902
6.80	86.771	12.30	103.073	17.70	171.933
6.90	87.182	12.40	103.452	17.80	175.080
7.00	87.582	12.50	103.843	17.90	178.346
7.10	87.970	12.60	104.247	18.00	181.735
7.20	88.348	12.70	104.665	18.10	185.251
7.30	88.716	12.80	105.097	18.20	188.897
7.40	89.074	12.90	105.545	18.30	192.678
7.50	89.424	13.00	106.009	18.40	196.598
7.60	89.764	13.10	106.490	18.50	200.661
7.70	90.097	13.20	106.990	18.60	204.871
7.80	90.422	13.30	107.508	18.70	209.233
7.90	90.739	13.40	108.046	18.80	213.751
8.00	91.409	13.50	108.606	18.90	218.430
8.10	91.953	13.60	109.187	19.00	223.275
8.20	91.651	13.70	109.792	19.10	228.291
8.30	91.943	13.80	110.422	19.20	233.481
8.40	92.230	13.90	111.077	19.30	238.852
8.50	92.512	14.00	111.759	19.40	244.408
8.60	92.789	14.10	112.469	19.50	250.154
8.70	93.062	14.20	113.209	19.60	256.096
8.90	93.596	14.30	113.980	19.70	262.239
9.00	93.859	14.40	114.783	19.80	268.588
9.10	94.118	14.50	115.619	19.90	275.149
9.20	94.375	14.60	116.492	20.00	281.927
9.30	94.631	14.70	117.401	20.10	288.928
9.40	94.884	14.80	118.348	20.20	296.158
9.50	95.136	14.90	119.336	20.30	303.623
9.60	95.386	15.00	120.366	20.40	311.327
9.70	95.636	15.10	121.440	20.50	319.278

P-ρ-T Table for Carbon Dioxide

Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)
Temperature = 318.15 K (continued)					
20.60	327.482	22.10	485.111	23.60	723.627
20.70	335.943	22.20	498.227	23.70	743.025
20.80	344.669	22.30	511.708	23.80	762.907
20.90	353.666	22.40	525.561	23.90	783.280
21.00	362.940	22.50	539.794	24.00	804.155
21.10	372.497	22.60	554.415	24.10	825.540
21.20	382.345	22.70	569.431	24.20	847.444
21.30	392.488	22.80	584.849	24.30	869.877
21.40	402.935	22.90	600.677	24.40	892.847
21.50	413.691	23.00	616.924	24.50	916.364
21.60	424.764	23.10	633.596	24.60	940.437
21.70	436.159	23.20	650.702	24.70	965.077
21.80	447.885	23.30	668.250	24.80	990.294
21.90	459.948	23.40	686.248	24.90	1016.096
22.00	472.354	23.50	704.704	25.00	1042.495
Temperature = 323.15 K					
0.20	5.266	3.90	69.936	7.60	95.491
0.30	7.819	4.00	70.996	7.70	95.918
0.40	10.320	4.10	72.027	7.80	96.337
0.50	12.768	4.20	73.032	7.90	96.749
0.60	15.166	4.30	74.011	8.00	97.155
0.70	17.513	4.40	74.965	8.10	97.554
0.80	19.810	4.50	75.894	8.20	97.947
0.90	22.057	4.60	76.798	8.30	98.334
1.00	24.256	4.70	77.679	8.40	98.716
1.10	26.407	4.80	78.537	8.50	99.094
1.20	28.511	4.90	79.372	8.60	99.467
1.30	30.568	5.00	80.186	8.70	99.836
1.40	32.579	5.10	80.978	8.80	100.201
1.50	34.544	5.20	81.750	8.90	100.564
1.60	36.465	5.30	82.502	9.00	100.923
1.70	38.342	5.40	83.235	9.10	101.280
1.80	40.176	5.50	83.948	9.20	101.635
1.90	41.967	5.60	84.643	9.30	101.988
2.00	43.716	5.70	85.320	9.40	102.340
2.10	45.424	5.80	85.980	9.50	102.691
2.20	47.092	5.90	86.624	9.60	103.042
2.30	48.720	6.00	87.251	9.70	103.392
2.40	50.309	6.10	87.862	9.80	103.743
2.50	51.860	6.20	88.458	9.90	104.094
2.60	53.373	6.30	89.040	10.00	104.447
2.70	54.849	6.40	89.607	10.10	104.801
2.80	56.289	6.50	90.161	10.20	105.157
2.90	57.693	6.60	90.702	10.30	105.515
3.00	59.063	6.70	91.230	10.40	105.876
3.10	60.398	6.80	91.746	10.50	106.240
3.20	61.700	6.90	92.250	10.60	106.608
3.30	62.970	7.00	92.743	10.70	106.980
3.40	64.207	7.10	93.225	10.80	107.357
3.50	65.413	7.20	93.697	10.90	107.738
3.60	66.588	7.30	94.159	11.00	108.125
3.70	67.733	7.40	94.612	11.20	108.918
3.80	68.849	7.50	95.055	11.30	109.325

P-ρ-T Table for Carbon Dioxide

Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)
Temperature = 323.15 K (continued)					
11.40	109.740	16.00	151.606	20.60	362.593
11.50	110.162	16.10	153.492	20.70	371.536
11.60	110.593	16.20	155.448	20.80	380.747
11.70	111.034	16.30	157.478	20.90	390.235
11.80	111.485	16.40	159.584	21.00	400.004
11.90	111.946	16.50	161.770	21.10	410.061
12.00	112.419	16.60	164.036	21.20	420.412
12.10	112.903	16.70	166.388	21.30	431.065
12.20	113.400	16.80	168.826	21.40	442.025
12.30	113.911	16.90	171.355	21.50	453.300
12.40	114.436	17.00	173.977	21.60	464.895
12.50	114.975	17.10	176.696	21.70	476.819
12.60	115.530	17.20	179.514	21.80	489.077
12.70	116.101	17.30	182.435	21.90	501.676
12.80	116.690	17.40	185.461	22.00	514.624
12.90	117.297	17.50	188.598	22.10	527.928
13.00	117.923	17.60	191.847	22.20	541.595
13.10	118.569	17.70	195.213	22.30	555.632
13.20	119.236	17.80	198.699	22.40	570.046
13.30	119.924	17.90	202.309	22.50	584.846
13.40	120.636	18.00	206.046	22.60	600.037
13.50	121.372	18.10	209.916	22.70	615.629
13.60	122.133	18.20	213.920	22.80	631.628
13.70	122.920	18.30	218.065	22.90	648.043
13.80	123.735	18.40	222.353	23.00	664.880
13.90	124.578	18.50	226.789	23.10	682.149
14.00	125.452	18.60	231.378	23.20	699.857
14.10	126.356	18.70	236.123	23.30	718.013
14.20	127.294	18.80	241.030	23.40	736.623
14.30	128.265	18.90	246.102	23.50	755.698
14.40	129.272	19.00	251.345	23.60	775.246
14.50	130.316	19.10	256.764	23.70	795.274
14.60	131.399	19.20	262.363	23.80	815.791
14.70	132.521	19.30	268.147	23.90	836.808
14.80	133.686	19.40	274.121	24.00	858.331
14.90	134.894	19.50	280.290	24.10	880.371
15.00	136.148	19.60	286.660	24.20	902.937
15.10	137.448	19.70	293.236	24.30	926.037
15.20	138.798	19.80	300.023	24.40	949.682
15.30	140.199	19.90	307.027	24.50	973.881
15.40	141.652	20.00	314.253	24.60	998.644
15.50	143.161	20.10	321.706	24.70	1023.980
15.60	144.727	20.20	329.393	24.80	1049.901
15.70	146.352	20.30	337.320	24.90	1076.415
15.80	148.039	20.40	345.491	25.00	1103.533
15.90	149.789	20.50	353.914		
Temperature = 328.15 K					
0.20	5.351	0.80	20.178	1.40	33.269
0.30	7.949	0.90	22.477	1.50	35.291
0.40	10.495	1.00	24.728	1.60	37.271
0.50	12.990	1.10	26.932	1.70	39.207
0.60	15.435	1.20	29.089	1.80	41.101
0.70	17.831	1.30	31.201	1.90	72.953

P-ρ-T Table for Carbon Dioxide

Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)
Temperature = 328.15 K (continued)					
2.00	44.765	7.40	100.091	12.80	128.411
2.10	46.536	7.50	100.629	12.90	129.180
2.20	48.268	7.60	101.160	13.00	129.970
2.30	49.961	7.70	101.682	13.10	130.782
2.40	51.616	7.80	102.197	13.20	131.619
2.50	53.234	7.90	102.706	13.30	132.480
2.60	54.815	8.00	103.207	13.40	133.366
2.70	56.360	8.10	103.703	13.50	134.280
2.80	57.869	8.20	104.193	13.60	135.221
2.90	59.344	8.30	104.677	13.70	136.192
3.00	60.785	8.40	105.157	13.80	137.193
3.10	62.192	8.50	105.633	13.90	138.225
3.20	63.567	8.60	106.104	14.00	139.291
3.30	64.911	8.70	106.572	14.10	140.390
3.40	66.222	8.80	107.036	14.20	141.526
3.50	67.504	8.90	107.498	14.30	142.698
3.60	68.755	9.00	107.958	14.40	142.909
3.70	69.977	9.10	108.415	14.50	145.160
3.80	71.170	9.20	108.872	14.60	146.453
3.90	72.336	9.30	109.327	14.70	147.789
4.00	73.474	9.40	109.781	14.80	149.171
4.10	74.585	9.50	110.235	14.90	150.599
4.20	75.671	9.60	110.690	15.00	152.076
4.30	76.731	9.70	111.145	15.10	153.603
4.40	77.766	9.80	111.602	15.20	155.183
4.50	78.777	9.90	112.059	15.30	156.817
4.60	79.764	10.00	112.519	15.40	158.508
4.70	80.728	10.10	112.982	15.50	160.257
4.80	81.670	10.20	113.447	15.60	162.067
4.90	82.590	10.30	113.916	15.70	163.940
5.00	83.489	10.40	114.389	15.80	165.878
5.10	84.368	10.50	114.867	15.90	167.884
5.20	85.226	10.60	115.349	16.00	169.960
5.30	86.064	10.70	115.837	16.10	172.108
5.40	86.884	10.80	116.331	16.20	174.332
5.50	87.685	10.90	116.831	16.30	176.633
5.60	88.468	11.00	117.339	16.40	179.014
5.70	89.234	11.10	117.854	16.50	181.478
5.80	89.984	11.20	118.378	16.60	184.028
5.90	90.716	11.30	118.910	16.70	186.666
6.00	91.434	11.40	119.452	16.80	189.396
6.10	92.135	11.50	120.004	16.90	192.221
6.20	92.822	11.60	120.566	17.00	195.143
6.30	93.495	11.70	121.141	17.10	198.116
6.40	94.154	11.80	121.727	17.20	201.293
6.50	94.800	11.90	122.326	17.30	204.527
6.60	95.433	12.00	122.938	17.40	207.872
6.70	96.053	12.10	123.564	17.50	211.331
6.80	96.662	12.20	124.206	17.60	214.907
6.90	97.259	12.30	124.863	17.70	218.605
7.00	97.846	12.40	125.536	17.80	222.428
7.10	98.421	12.50	126.227	17.90	226.379
7.20	98.987	12.60	126.396	18.00	230.462
7.30	99.544	12.70	127.664	18.10	234.682



P-ρ-T Table for Carbon Dioxide

Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)
Temperature = 328.15 K (continued)					
18.20	239.042	20.50	388.538	22.80	678.268
18.30	243.546	20.60	397.688	22.90	695.264
18.40	248.199	20.70	407.106	23.00	712.689
18.50	253.005	20.80	416.797	23.10	730.550
18.60	257.696	20.90	426.769	23.20	748.856
18.70	263.093	21.00	437.027	23.30	767.615
18.80	268.384	21.10	447.578	23.40	786.835
18.90	273.846	21.20	458.428	23.50	806.525
19.00	279.483	21.30	469.584	23.60	826.693
19.10	285.301	21.40	481.052	23.70	847.348
19.20	291.303	21.50	492.839	23.80	868.499
19.30	297.496	21.60	504.951	23.90	890.155
19.40	303.883	21.70	517.397	24.00	912.324
19.50	310.471	21.80	530.181	24.10	935.017
19.60	317.264	21.90	543.312	24.20	958.241
19.70	324.267	22.00	556.797	24.30	982.008
19.80	331.487	22.10	570.642	24.40	1006.326
19.90	338.928	22.20	584.855	24.50	1031.205
20.00	346.596	22.30	599.442	24.60	1056.655
20.10	354.496	22.40	614.413	24.70	1082.686
20.20	362.635	22.50	629.773	24.80	1109.308
20.30	371.017	22.60	645.530	24.90	1136.533
20.40	379.650	22.70	661.693	25.00	1164.369
Temperature = 333.15 K					
0.20	5.437	3.10	63.972	6.00	95.572
0.30	8.078	3.20	65.419	6.10	96.363
0.40	10.670	3.30	66.835	6.20	97.140
0.50	13.212	3.40	68.220	6.30	97.903
0.60	15.704	3.50	69.575	6.40	98.653
0.70	18.149	3.60	70.902	6.50	99.391
0.80	20.545	3.70	72.200	6.60	100.115
0.90	22.895	3.80	73.469	6.70	100.828
1.00	25.197	3.90	74.712	6.80	101.529
1.10	27.454	4.00	75.928	6.90	102.220
1.20	29.666	4.10	77.118	7.00	102.900
1.30	31.832	4.20	78.283	7.10	103.569
1.40	33.955	4.30	79.422	7.20	104.229
1.50	36.035	4.40	80.538	7.30	104.880
1.60	38.072	4.50	81.630	7.40	105.523
1.70	40.067	4.60	82.699	7.50	106.157
1.80	42.021	4.70	83.746	7.60	106.783
1.90	43.934	4.80	84.771	7.70	107.402
2.00	45.807	4.90	85.775	7.80	108.013
2.10	47.641	5.00	86.758	7.90	108.619
2.20	49.437	5.10	87.720	8.00	109.218
2.30	51.194	5.20	88.664	8.10	109.811
2.40	52.914	5.30	89.588	8.20	110.400
2.50	54.598	5.40	90.494	8.30	110.983
2.60	56.246	5.50	91.382	8.40	111.562
2.70	57.859	5.60	92.253	8.50	112.137
2.80	59.437	5.70	93.106	8.60	112.709
2.90	60.982	5.80	93.944	8.70	113.278
3.00	62.493	5.90	94.765	8.80	113.844

P-ρ-T Table for Carbon Dioxide

Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)
Temperature = 333.15 K (continued)					
8.90	114.408	14.30	157.237	19.70	355.315
9.00	114.970	14.40	158.652	19.80	362.962
9.10	115.531	14.50	160.111	19.90	370.836
9.20	116.091	14.60	161.614	20.00	378.941
9.30	116.651	14.70	163.164	20.10	387.283
9.40	117.211	14.80	164.763	20.20	395.868
9.50	117.772	14.90	166.411	20.30	404.702
9.60	118.333	15.00	168.111	20.40	413.790
9.70	118.897	15.10	169.866	20.50	423.139
9.80	119.462	15.20	171.676	20.60	432.754
9.90	120.030	15.30	173.543	20.70	442.641
10.00	120.601	15.40	175.471	20.80	452.807
10.10	121.175	15.50	177.461	20.90	463.258
10.20	121.754	15.60	179.515	21.00	474.000
10.30	122.337	15.70	181.636	21.10	485.039
10.40	122.925	15.80	183.825	21.20	496.382
10.50	123.519	15.90	186.086	21.30	508.036
10.60	124.120	16.00	188.421	21.40	520.006
10.70	124.727	16.10	190.832	21.50	532.301
10.80	125.342	16.20	193.321	21.60	544.926
10.90	125.965	16.30	195.892	21.70	557.888
11.00	126.596	16.40	198.548	21.80	571.194
11.10	127.237	16.50	201.290	21.90	584.851
11.20	127.888	16.60	204.122	22.00	598.867
11.30	128.549	16.70	207.047	22.10	613.248
11.40	129.222	16.80	210.068	22.20	628.002
11.50	129.906	16.90	213.187	22.30	643.136
11.60	130.603	17.00	216.409	22.40	658.658
11.70	131.314	17.10	219.735	22.50	674.574
11.80	132.038	17.20	223.169	22.60	690.894
11.90	132.777	17.30	226.715	22.70	707.623
12.00	133.532	17.40	230.376	22.80	724.771
12.10	134.303	17.50	234.156	22.90	742.344
12.20	135.091	17.60	238.058	23.00	760.352
12.30	135.897	17.70	242.085	23.10	778.802
12.40	136.721	17.80	246.242	23.20	797.702
12.50	137.566	17.90	250.531	23.30	814.061
12.60	138.430	18.00	254.958	23.40	836.887
12.70	139.316	18.10	259.526	23.50	857.189
12.80	140.224	18.20	264.238	23.60	877.975
12.90	141.156	18.30	269.100	23.70	899.254
13.00	142.111	18.40	274.115	23.80	921.036
13.10	143.092	18.50	279.288	23.90	943.328
13.20	144.099	18.60	284.622	24.00	966.141
13.30	145.133	18.70	290.123	24.10	989.484
13.40	146.196	18.80	295.795	24.20	1013.365
13.50	147.288	18.90	301.642	24.30	1037.796
13.60	148.411	19.00	307.669	24.40	1062.785
13.70	149.566	19.10	313.881	24.50	1088.342
13.80	150.753	19.20	320.283	24.60	1114.478
13.90	151.976	19.30	326.879	24.70	1141.202
14.00	153.234	19.40	333.676	24.80	1168.526
14.10	154.529	19.50	340.677	24.90	1196.459
14.20	155.863	19.60	347.888	25.00	1225.013

P-ρ-T Table for Carbon Dioxide

Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)
Temperature = 338.15 K					
0.20	5.522	5.60	96.001	11.00	135.886
0.30	8.208	5.70	96.942	11.10	136.655
0.40	10.845	5.80	97.867	11.20	137.436
0.50	13.433	5.90	98.776	11.30	138.229
0.60	15.973	6.00	99.671	11.40	139.034
0.70	18.466	6.10	100.552	11.50	139.854
0.80	20.912	6.20	101.418	11.60	140.687
0.90	23.311	6.30	102.272	11.70	141.536
1.00	25.665	6.40	103.112	11.80	142.104
1.10	27.975	6.50	103.941	11.90	143.282
1.20	30.240	6.60	104.757	12.00	144.181
1.30	32.461	6.70	105.562	12.10	145.099
1.40	34.639	6.80	106.356	12.20	146.035
1.50	36.775	6.90	107.139	12.30	146.992
1.60	38.870	7.00	107.912	12.40	147.969
1.70	40.923	7.10	108.676	12.50	148.968
1.80	42.936	7.20	109.431	12.60	149.990
1.90	44.910	7.30	110.177	12.70	151.036
2.00	46.844	7.40	110.914	12.80	152.106
2.10	48.740	7.50	111.644	12.90	153.201
2.20	50.598	7.60	112.367	13.00	154.324
2.30	52.419	7.70	113.082	13.10	155.473
2.40	54.204	7.80	113.792	13.20	156.652
2.50	55.954	7.90	114.495	13.30	157.860
2.60	57.668	8.00	115.193	13.40	159.100
2.70	59.348	8.10	115.885	13.50	160.371
2.80	60.994	8.20	116.573	13.60	161.676
2.90	62.607	8.30	117.257	13.70	163.016
3.00	64.188	8.40	117.937	13.80	164.391
3.10	65.737	8.50	118.613	13.90	165.804
3.20	67.256	8.60	119.287	14.00	167.255
3.30	68.743	8.70	119.958	14.10	168.746
3.40	70.201	8.80	120.628	14.20	170.279
3.50	71.630	8.90	121.296	14.30	171.855
3.60	73.031	9.00	121.963	14.40	173.476
3.70	74.404	9.10	122.629	14.50	175.142
3.80	75.749	9.20	123.296	14.60	176.857
3.90	77.068	9.30	123.963	14.70	178.621
4.00	78.361	9.40	124.630	14.80	180.437
4.10	79.628	9.50	125.300	14.90	182.306
4.20	80.871	9.60	125.971	15.00	184.230
4.30	82.090	9.70	126.645	15.10	186.211
4.40	83.285	9.80	127.322	15.20	188.252
4.50	84.458	9.90	128.002	15.30	190.353
4.60	85.607	10.00	128.687	15.40	192.518
4.70	86.736	10.10	129.376	15.50	194.749
4.80	87.842	10.20	130.070	15.60	197.047
4.90	88.929	10.30	130.771	15.70	199.415
5.00	89.995	10.40	131.477	15.80	201.856
5.10	91.042	10.50	132.191	15.90	204.372
5.20	92.069	10.60	132.912	16.00	206.965
5.30	93.078	10.70	133.642	16.10	209.639
5.40	94.070	10.80	134.380	16.20	212.394
5.50	95.044	10.90	135.128	16.30	215.236

P-p-T Table for Carbon Dioxide

Density, $\rho$ (mol/l)	Pressure, P (bar)	Density, $\rho$ (mol/l)	Pressure, P (bar)	Density, $\rho$ (mol/l)	Pressure, P (bar)
Temperature = 338.15 K (continued)					
16.40	218.165	19.30	356.283	22.20	671.037
16.50	221.185	19.40	363.484	22.30	686.713
16.60	224.299	19.50	370.895	22.40	702.782
16.70	227.509	19.60	378.520	22.50	719.251
16.80	230.820	19.70	386.365	22.60	736.128
16.90	234.233	19.80	394.436	22.70	753.421
17.00	237.752	19.90	402.737	22.80	771.137
17.10	241.380	20.00	411.275	22.90	789.285
17.20	245.121	20.10	420.054	23.00	807.872
17.30	248.978	20.20	429.081	23.10	826.907
17.40	252.954	20.30	438.362	23.20	846.399
17.50	257.052	20.40	447.901	23.30	866.355
17.60	261.277	20.50	457.705	23.40	886.784
17.70	265.632	20.60	467.781	23.50	907.695
17.80	270.121	20.70	478.133	23.60	929.096
17.90	274.748	20.80	488.769	23.70	950.997
18.00	279.515	20.90	499.694	23.80	973.407
18.10	284.429	21.00	510.914	23.90	996.334
18.20	289.491	21.10	522.437	24.00	1019.788
18.30	294.707	21.20	534.269	24.10	1043.779
18.40	300.082	21.30	546.416	24.20	1068.315
18.50	305.618	21.40	558.884	24.30	1093.408
18.60	311.320	21.50	571.681	24.40	1119.066
18.70	317.194	21.60	584.813	24.50	1145.301
18.80	323.242	21.70	598.287	24.60	1172.121
18.90	329.471	21.80	612.111	24.70	1199.537
19.00	335.885	21.90	626.290	24.80	1227.561
19.10	342.488	22.00	640.833	24.90	1256.202
19.20	349.286	22.10	655.746	25.00	1285.472
Temperature = 343.15 K					
0.20	5.607	2.50	57.301	4.80	90.888
0.30	8.337	2.60	59.081	4.90	92.056
0.40	11.019	2.70	60.827	5.00	93.205
0.50	13.654	2.80	62.541	5.10	94.335
0.60	16.241	2.90	64.222	5.20	95.446
0.70	18.782	3.00	65.872	5.30	96.539
0.80	21.277	3.10	67.491	5.40	97.615
0.90	23.727	3.20	69.080	5.50	98.675
1.00	26.132	3.30	70.639	5.60	99.718
1.10	28.494	3.40	72.169	5.70	100.745
1.20	30.812	3.50	73.670	5.80	101.757
1.30	33.087	3.60	75.144	5.90	102.754
1.40	35.321	3.70	76.591	6.00	103.737
1.50	37.513	3.80	78.011	6.10	104.706
1.60	39.664	3.90	79.405	6.20	105.662
1.70	41.775	4.00	80.774	6.30	106.605
1.80	43.847	4.10	82.119	6.40	107.536
1.90	45.880	4.20	83.439	6.50	108.445
2.00	47.875	4.30	84.736	6.60	109.363
2.10	49.833	4.40	86.010	6.70	110.259
2.20	51.753	4.50	87.261	6.80	111.146
2.30	53.638	4.60	88.491	6.90	112.022
2.40	55.487	4.70	89.700	7.00	112.889

P-ρ-T Table for Carbon Dioxide

Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)
Temperature = 343.15 K (continued)					
7.10	113.747	12.40	159.264	17.70	289.231
7.20	114.596	12.50	160.419	17.80	294.050
7.30	115.437	12.60	161.600	17.90	299.011
7.40	116.271	12.70	162.806	18.00	304.118
7.50	117.097	12.80	164.039	18.10	309.374
7.60	117.916	12.90	165.300	18.20	314.784
7.70	118.730	13.00	166.589	18.30	320.352
7.80	119.537	13.10	167.909	18.40	326.083
7.90	120.339	13.20	169.261	18.50	331.980
8.00	121.136	13.30	170.644	18.60	338.047
8.10	121.928	13.40	172.061	18.70	344.290
8.20	122.717	13.50	173.513	18.80	350.713
8.30	123.502	13.60	175.000	18.90	357.321
8.40	124.284	13.70	176.525	19.00	364.118
8.50	125.063	13.80	178.089	19.10	371.108
8.60	125.840	13.90	179.693	19.20	378.298
8.70	126.616	14.00	181.338	19.30	385.692
8.80	127.390	14.10	183.026	19.40	393.294
8.90	128.163	14.20	184.758	19.50	401.110
9.00	128.937	14.30	186.536	19.60	409.146
9.10	129.710	14.40	188.362	19.70	417.406
9.20	130.485	14.50	190.238	19.80	425.896
9.30	131.261	14.60	192.164	19.90	434.621
9.40	132.038	14.70	194.143	20.00	443.587
9.50	132.819	14.80	196.176	20.10	452.800
9.60	133.602	14.90	198.266	20.20	462.264
9.70	134.388	15.00	200.414	20.30	471.987
9.80	135.179	15.10	202.623	20.40	481.973
9.90	135.974	15.20	204.894	20.50	492.229
10.00	136.774	15.30	207.229	20.60	502.760
10.10	137.580	15.40	209.632	20.70	513.573
10.20	138.393	15.50	212.103	20.80	524.674
10.30	139.212	15.60	214.646	20.90	536.069
10.40	140.039	15.70	217.262	21.00	547.764
10.50	140.875	15.80	219.954	21.10	559.767
10.60	141.719	15.90	222.725	21.20	572.082
10.70	142.573	16.00	225.577	21.30	584.718
10.80	143.437	16.10	228.512	21.40	597.680
10.90	144.313	16.20	231.534	21.50	610.975
11.00	145.199	16.30	234.645	21.60	624.611
11.10	146.099	16.40	237.848	21.70	638.593
11.20	147.011	16.50	241.145	21.80	652.929
11.30	147.937	16.60	244.540	21.90	667.627
11.40	148.878	16.70	248.036	22.00	682.693
11.50	149.834	16.80	251.635	22.10	698.134
11.60	150.806	16.90	255.341	22.20	713.958
11.70	151.795	17.00	259.157	22.30	730.173
11.80	152.802	17.10	263.086	22.40	746.785
11.90	153.828	17.20	267.132	22.50	763.803
12.00	154.873	17.30	271.298	22.60	781.235
12.10	155.938	17.40	275.587	22.70	799.087
12.20	157.024	17.50	280.003	22.80	817.369
12.30	158.133	17.60	284.550	22.90	836.088

P-ρ-T Table for Carbon Dioxide

Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)
Temperature = 343.15 K (continued)					
23.00	855.252	23.70	1002.582	24.40	1175.178
23.10	874.869	23.80	1025.617	24.50	1202.088
23.20	894.949	23.90	1049.177	24.60	1229.591
23.30	915.500	24.00	1073.271	24.70	1257.699
23.40	936.529	24.10	1097.908	24.80	1286.421
23.50	958.047	24.20	1123.098	24.90	1315.770
23.60	980.061	24.30	1148.851	25.00	1345.755
Temperature = 348.15 K					
0.20	5.692	4.60	91.354	9.00	135.893
0.30	8.467	4.70	92.642	9.10	136.775
0.40	11.194	4.80	93.911	9.20	137.659
0.50	13.874	4.90	95.160	9.30	138.545
0.60	16.508	5.00	96.391	9.40	139.434
0.70	19.097	5.10	97.603	9.50	140.326
0.80	21.642	5.20	98.797	9.60	141.223
0.90	24.142	5.30	99.974	9.70	142.123
1.00	26.598	5.40	101.134	9.80	143.029
1.10	29.011	5.50	102.278	9.90	143.941
1.20	31.382	5.60	103.406	10.00	144.859
1.30	33.712	5.70	104.519	10.10	145.784
1.40	36.000	5.80	105.618	10.20	146.716
1.50	38.247	5.90	106.702	10.30	147.657
1.60	40.455	6.00	107.773	10.40	148.606
1.70	42.624	6.10	108.830	10.50	149.565
1.80	44.754	6.20	109.875	10.60	150.534
1.90	46.847	6.30	110.907	10.70	151.514
2.00	48.902	6.40	111.928	10.80	152.506
2.10	50.920	6.50	112.938	10.90	153.510
2.20	52.902	6.60	113.936	11.00	154.528
2.30	54.850	6.70	114.925	11.10	155.559
2.40	56.762	6.80	115.904	11.20	156.605
2.50	58.641	6.90	116.873	11.30	157.666
2.60	60.486	7.00	117.833	11.40	158.743
2.70	62.298	7.10	118.785	11.50	159.838
2.80	64.078	7.20	119.729	11.60	160.950
2.90	65.827	7.30	120.666	11.70	162.081
3.00	67.545	7.40	121.595	11.80	163.231
3.10	69.233	7.50	122.518	11.90	164.402
3.20	70.892	7.60	123.435	12.00	165.595
3.30	72.521	7.70	124.346	12.10	166.809
3.40	74.122	7.80	125.252	12.20	168.047
3.50	75.696	7.90	126.154	12.30	169.308
3.60	77.243	8.00	127.051	12.40	170.595
3.70	78.763	8.10	127.944	12.50	171.908
3.80	80.257	8.20	128.834	12.60	173.247
3.90	81.726	8.30	129.721	12.70	174.615
4.00	83.171	8.40	130.606	12.80	176.012
4.10	84.591	8.50	131.489	12.90	177.439
4.20	85.988	8.60	132.370	13.00	178.898
4.30	87.362	8.70	133.251	13.10	180.389
4.40	88.714	8.80	134.131	13.20	181.913
4.50	90.045	8.90	135.011	13.30	183.472

P-ρ-T Table for Carbon Dioxide

Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)
Temperature = 348.15 K (continued)					
13.40	185.068	17.30	293.662	21.20	609.818
13.50	186.700	17.40	298.263	21.30	622.938
13.60	188.371	17.50	302.995	21.40	636.390
13.70	190.083	17.60	307.862	21.50	650.180
13.80	191.835	17.70	312.867	21.60	664.315
13.90	193.630	17.80	318.014	21.70	678.802
14.00	195.470	17.90	323.307	21.80	693.648
14.10	197.355	18.00	328.751	21.90	708.860
14.20	199.287	18.10	334.348	22.00	724.445
14.30	201.269	18.20	340.104	22.10	740.411
14.40	203.300	18.30	346.021	22.20	756.765
14.50	205.384	18.40	352.105	22.30	773.515
14.60	207.522	18.50	358.360	22.40	790.668
14.70	209.716	18.60	364.791	22.50	808.232
14.80	211.968	18.70	371.401	22.60	826.215
14.90	214.279	18.80	378.195	22.70	844.624
15.00	216.652	18.90	385.178	22.80	863.468
15.10	219.088	19.00	392.355	22.90	882.755
15.20	221.590	19.10	399.730	23.00	902.493
15.30	224.160	19.20	407.308	23.10	922.691
15.40	226.800	19.30	415.095	23.20	943.357
15.50	229.512	19.40	423.095	23.30	964.499
15.60	232.299	19.50	431.314	23.40	986.127
15.70	235.163	19.60	439.756	23.50	1008.249
15.80	238.106	19.70	448.427	23.60	1030.875
15.90	241.132	19.80	457.333	23.70	1054.012
16.00	244.242	19.90	466.478	23.80	1077.672
16.10	247.439	20.00	475.869	23.90	1101.863
16.20	250.727	20.10	485.511	24.00	1126.595
16.30	254.107	20.20	495.409	24.10	1151.877
16.40	257.582	20.30	505.570	24.20	1177.719
16.50	261.156	20.40	515.999	24.30	1204.132
16.60	264.832	20.50	526.702	24.40	1231.125
16.70	268.612	20.60	537.685	24.50	1258.710
16.80	272.499	20.70	548.955	24.60	1286.896
16.90	276.497	20.80	560.517	24.70	1315.693
17.00	280.609	20.90	572.378	24.80	1345.114
17.10	284.838	21.00	584.545	24.90	1375.169
17.20	289.188	21.10	597.022	25.00	1405.870
Temperature = 353.15 K					
0.20	5.777	1.40	36.676	2.60	61.883
0.30	8.596	1.50	38.979	2.70	63.761
0.40	11.368	1.60	41.244	2.80	65.607
0.50	14.094	1.70	43.469	2.90	67.423
0.60	16.776	1.80	45.658	3.00	69.209
0.70	19.412	1.90	47.809	3.10	70.966
0.80	22.005	2.00	49.923	3.20	72.693
0.90	24.555	2.10	52.002	3.30	74.393
1.00	27.062	2.20	54.046	3.40	76.064
1.10	29.527	2.30	56.056	3.50	77.709
1.20	31.951	2.40	58.031	3.60	79.328
1.30	34.334	2.50	59.973	3.70	80.921

P-ρ-T Table for Carbon Dioxide

Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)
Temperature = 353.15 K (continued)					
3.80	82.488	9.00	142.830	14.30	216.042
3.90	84.032	9.10	143.822	14.40	218.280
4.00	85.551	9.20	144.816	14.50	220.573
4.10	87.047	9.30	145.814	14.60	222.924
4.20	88.520	9.40	146.816	14.70	225.333
4.30	89.971	9.50	147.822	14.80	227.803
4.40	91.400	9.60	148.832	14.90	230.335
4.50	92.809	9.70	149.849	15.00	232.933
4.60	94.196	9.80	150.872	15.10	235.597
4.70	95.564	9.90	151.901	15.20	238.330
4.80	96.913	10.00	152.938	15.30	241.134
4.90	98.243	10.10	153.983	15.40	244.011
5.00	99.554	10.20	155.036	15.50	246.964
5.10	100.848	10.30	156.100	15.60	249.996
5.20	102.125	10.40	157.176	15.70	253.107
5.30	103.385	10.50	158.257	15.80	256.302
5.40	104.628	10.60	159.353	15.90	259.582
5.50	105.857	10.70	160.460	16.00	262.950
5.60	107.070	10.80	161.581	16.10	266.409
5.70	108.268	10.90	162.716	16.20	269.961
5.80	109.453	11.00	163.865	16.30	273.610
5.90	110.624	11.10	165.030	16.40	277.358
6.00	111.781	11.20	166.211	16.50	281.208
6.10	112.927	11.30	167.408	16.60	285.163
6.20	114.060	11.40	168.624	16.70	289.277
6.30	115.182	11.50	169.858	16.80	293.401
6.40	116.292	11.60	171.112	16.90	297.690
6.50	117.392	11.70	172.386	17.00	302.097
6.60	118.482	11.80	173.681	17.10	306.625
6.70	119.562	11.90	174.999	17.20	311.277
6.80	120.633	12.00	176.340	17.30	316.057
6.90	121.695	12.10	177.704	17.40	320.968
7.00	122.749	12.20	179.094	17.50	326.015
7.10	123.795	12.30	180.510	17.60	331.200
7.20	124.834	12.40	181.953	17.70	336.528
7.30	125.866	12.50	183.424	17.80	342.001
7.40	126.892	12.60	184.925	17.90	347.625
7.50	127.911	12.70	186.455	18.00	353.403
7.60	128.926	12.80	188.017	18.10	359.340
7.70	129.935	12.90	189.611	18.20	365.438
7.80	130.940	13.00	191.239	18.30	371.703
7.90	131.941	13.10	192.902	18.40	378.139
8.00	132.939	13.20	194.600	18.50	384.749
8.10	133.933	13.30	196.336	18.60	391.539
8.20	134.925	13.40	198.111	18.70	398.513
8.30	135.915	13.50	199.925	18.80	405.676
8.40	136.904	13.60	201.780	18.90	413.032
8.50	137.891	13.70	203.678	19.00	420.586
8.60	138.878	13.80	205.620	19.10	428.342
8.70	139.864	13.90	207.607	19.20	436.306
8.80	140.852	14.00	209.642	19.30	444.483
8.90	141.840	14.10	211.724	19.40	452.878
9.00	142.830	14.20	213.857	19.50	461.496



P-ρ-T Table for Carbon Dioxide

Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)
Temperature = 353.15 K (continued)					
19.60	470.341	21.50	689.294	23.40	1035.581
19.70	479.420	21.60	703.925	23.50	1058.306
19.80	488.738	21.70	718.913	23.60	1081.541
19.90	498.300	21.80	734.265	23.70	1105.295
20.00	508.112	21.90	749.989	23.80	1129.577
20.10	518.180	22.00	766.090	23.90	1154.397
20.20	528.508	22.10	782.578	24.00	1179.765
20.30	539.104	22.20	799.459	24.10	1205.691
20.40	549.972	22.30	816.741	24.20	1232.185
20.50	561.119	22.40	834.431	24.30	1259.256
20.60	572.551	22.50	852.538	24.40	1286.915
20.70	584.274	22.60	871.070	24.50	1315.173
20.80	596.294	22.70	890.033	24.60	1344.040
20.90	608.617	22.80	909.437	24.70	1373.528
21.00	621.251	22.90	929.290	24.80	1403.646
21.10	634.200	23.00	949.600	24.90	1434.407
21.20	647.473	23.10	970.375	25.00	1465.822
21.30	661.075	23.20	991.625		
21.40	675.013	23.30	1013.357		
Temperature = 363.15 K					
0.20	5.947	3.30	78.104	6.40	124.945
0.30	8.854	3.40	79.916	6.50	126.225
0.40	11.716	3.50	81.702	6.60	127.497
0.50	14.534	3.60	83.463	6.70	128.759
0.60	17.309	3.70	85.200	6.80	130.014
0.70	20.041	3.80	86.912	6.90	131.262
0.80	22.731	3.90	88.602	7.00	132.503
0.90	25.380	4.00	90.269	7.10	133.737
1.00	27.988	4.10	91.914	7.20	134.966
1.10	30.556	4.20	93.538	7.30	136.189
1.20	33.084	4.30	95.141	7.40	137.408
1.30	35.573	4.40	96.723	7.50	138.622
1.40	38.024	4.50	98.286	7.60	139.832
1.50	40.436	4.60	99.830	7.70	141.038
1.60	42.812	4.70	101.355	7.80	142.242
1.70	45.151	4.80	102.862	7.90	143.444
1.80	47.454	4.90	104.351	8.00	144.643
1.90	49.722	5.00	105.823	8.10	145.841
2.00	51.955	5.10	107.279	8.20	147.039
2.10	54.154	5.20	108.719	8.30	148.236
2.20	56.319	5.30	110.144	8.40	149.433
2.30	58.452	5.40	111.553	8.50	150.631
2.40	60.552	5.50	112.949	8.60	151.830
2.50	62.620	5.60	114.330	8.70	153.030
2.60	64.658	5.70	115.698	8.80	154.234
2.70	66.665	5.80	117.054	8.90	155.440
2.80	68.643	5.90	118.397	9.00	156.649
2.90	70.591	6.00	119.728	9.10	157.863
3.00	72.510	6.10	121.048	9.20	159.081
3.10	74.402	6.20	122.357	9.30	160.305
3.20	76.267	6.30	123.656	9.40	161.534

P-p-T Table for Carbon Dioxide

Density, $\rho$ (mol/l)	Pressure, P (bar)	Density, $\rho$ (mol/l)	Pressure, P (bar)	Density, $\rho$ (mol/l)	Pressure, P (bar)
Temperature = 363.15 K (continued)					
9.50	162.770	14.70	256.664	19.90	561.815
9.60	164.013	14.80	259.571	20.00	572.460
9.70	165.264	14.90	262.546	20.10	583.370
9.80	166.523	15.00	265.593	20.20	594.549
9.90	167.792	15.10	268.713	20.30	606.005
10.00	169.070	15.20	271.908	20.40	617.742
10.10	170.358	15.30	275.180	20.50	629.768
10.20	171.658	15.40	278.532	20.60	642.087
10.30	172.970	15.50	281.967	20.70	654.707
10.40	174.294	15.60	285.486	20.80	667.633
10.50	175.632	15.70	289.092	20.90	680.872
10.60	176.984	15.80	292.787	21.00	694.430
10.70	178.351	15.90	296.575	21.10	708.314
10.80	179.734	16.00	300.458	21.20	722.531
10.90	181.133	16.10	304.438	21.30	737.086
11.00	182.550	16.20	308.519	21.40	751.988
11.10	183.985	16.30	312.703	21.50	767.243
11.20	185.439	16.40	316.994	21.60	782.857
11.30	186.913	16.50	321.393	21.70	798.839
11.40	188.409	16.60	325.905	21.80	815.195
11.50	189.926	16.70	330.533	21.90	831.932
11.60	191.466	16.80	335.279	22.00	849.059
11.70	193.030	16.90	340.146	22.10	866.581
11.80	194.618	17.00	345.139	22.20	884.508
11.90	196.233	17.10	350.261	22.30	902.847
12.00	197.874	17.20	355.514	22.40	921.605
12.10	199.542	17.30	360.903	22.50	940.791
12.20	201.240	17.40	366.431	22.60	960.413
12.30	202.968	17.50	372.101	22.70	980.478
12.40	204.727	17.60	377.918	22.80	1000.995
12.50	206.517	17.70	383.886	22.90	1021.973
12.60	208.341	17.80	390.007	23.00	1043.421
12.70	210.200	17.90	396.287	23.10	1065.345
12.80	212.094	18.00	402.728	23.20	1087.757
12.90	214.025	18.10	409.336	23.30	1110.664
13.00	215.994	18.20	416.114	23.40	1134.075
13.10	218.003	18.30	423.067	23.50	1158.001
13.20	220.052	18.40	430.199	23.60	1182.449
13.30	222.143	18.50	437.513	23.70	1207.430
13.40	224.278	18.60	445.016	23.80	1232.954
13.50	226.457	18.70	452.711	23.90	1259.029
13.60	228.682	18.80	460.603	24.00	1285.667
13.70	230.956	18.90	468.697	24.10	1312.876
13.80	233.278	19.00	476.997	24.20	1340.669
13.90	235.651	19.10	485.508	24.30	1369.054
14.00	238.077	19.20	494.236	24.40	1398.042
14.10	240.556	19.30	503.184	24.50	1427.645
14.20	243.091	19.40	512.360	24.60	1457.873
14.30	245.684	19.50	521.766	24.70	1488.738
14.40	248.335	19.60	531.410	24.80	1520.250
14.50	251.048	19.70	541.295	24.90	1552.421
14.60	253.823	19.80	551.429	25.00	1585.264

P-ρ-T Table for Carbon Dioxide

Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)
Temperature = 373.15 K					
0.20	6.117	5.60	121.514	11.00	201.225
0.30	9.111	5.70	123.050	11.10	202.935
0.40	12.063	5.80	124.575	11.20	204.666
0.50	14.972	5.90	126.089	11.30	206.421
0.60	17.840	6.00	127.593	11.40	208.200
0.70	20.667	6.10	129.086	11.50	210.004
0.80	23.454	6.20	130.571	11.60	211.834
0.90	26.202	6.30	132.046	11.70	213.691
1.00	28.910	6.40	133.513	11.80	215.577
1.10	31.579	6.50	134.972	11.90	217.491
1.20	34.211	6.60	136.424	12.00	219.436
1.30	36.806	6.70	137.869	12.10	221.413
1.40	39.363	6.80	139.307	12.20	223.422
1.50	41.885	6.90	140.740	12.30	225.465
1.60	44.371	7.00	142.167	12.40	227.543
1.70	46.822	7.10	143.590	12.50	229.656
1.80	49.239	7.20	145.008	12.60	231.807
1.90	51.622	7.30	146.423	12.70	233.997
2.00	53.971	7.40	147.834	12.80	236.227
2.10	56.289	7.50	149.242	12.90	238.497
2.20	58.574	7.60	150.648	13.00	240.811
2.30	60.828	7.70	152.053	13.10	243.168
2.40	63.052	7.80	153.456	13.20	245.570
2.50	65.245	7.90	154.858	13.30	248.019
2.60	67.409	8.00	156.261	13.40	250.516
2.70	69.544	8.10	157.664	13.50	253.062
2.80	71.651	8.20	159.067	13.60	255.660
2.90	73.729	8.30	160.472	13.70	258.310
3.00	75.781	8.40	161.880	13.80	261.015
3.10	77.807	8.50	163.289	13.90	263.775
3.20	79.806	8.60	164.702	14.00	266.593
3.30	81.780	8.70	166.119	14.10	269.471
3.40	83.729	8.80	167.540	14.20	272.409
3.50	85.655	8.90	168.966	14.30	275.410
3.60	87.556	9.00	170.398	14.40	278.476
3.70	89.435	9.10	171.835	14.50	281.609
3.80	91.291	9.20	173.280	14.60	284.810
3.90	93.126	9.30	174.731	14.70	288.081
4.00	94.939	9.40	176.191	14.80	291.426
4.10	96.731	9.50	177.660	14.90	294.845
4.20	98.503	9.60	179.138	15.00	298.340
4.30	100.256	9.70	180.626	15.10	301.915
4.40	101.990	9.80	182.125	15.20	305.571
4.50	103.705	9.90	183.635	15.30	309.311
4.60	105.403	10.00	185.157	15.40	313.137
4.70	107.083	10.10	186.693	15.50	317.051
4.80	108.746	10.20	188.242	15.60	321.056
4.90	110.393	10.30	189.806	15.70	325.155
5.00	112.025	10.40	191.385	15.80	329.350
5.10	113.641	10.50	192.980	15.90	333.643
5.20	115.243	10.60	194.592	16.00	338.038
5.30	116.830	10.70	196.221	16.10	342.537
5.40	118.404	10.80	197.869	16.20	347.144
5.50	119.965	10.90	199.537	16.30	351.861

P-ρ-T Table for Carbon Dioxide

Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)
Temperature = 373.15 K (continued)					
16.40	356.690	19.30	561.744	22.20	969.115
16.50	361.636	19.40	571.690	22.30	988.502
16.60	366.701	19.50	581.875	22.40	1008.320
16.70	371.888	19.60	592.306	22.50	1028.576
16.80	377.201	19.70	602.988	22.60	1049.280
16.90	382.643	19.80	613.926	22.70	1070.440
17.00	388.217	19.90	625.126	22.80	1092.063
17.10	393.927	20.00	636.593	22.90	1114.159
17.20	399.776	20.10	648.334	23.00	1136.737
17.30	405.768	20.20	660.354	23.10	1159.805
17.40	411.907	20.30	672.658	23.20	1183.372
17.50	418.196	20.40	685.254	23.30	1207.447
17.60	424.638	20.50	698.147	23.40	1232.041
17.70	431.239	20.60	711.343	23.50	1257.161
17.80	438.001	20.70	724.848	23.60	1282.818
17.90	444.929	20.80	738.669	23.70	1309.022
18.00	452.027	20.90	752.813	23.80	1335.782
18.10	459.299	21.00	767.285	23.90	1363.108
18.20	466.749	21.10	782.093	24.00	1391.012
18.30	474.382	21.20	797.243	24.10	1419.502
18.40	482.201	21.30	812.742	24.20	1448.589
18.50	490.212	21.40	828.597	24.30	1478.285
18.60	498.419	21.50	844.815	24.40	1508.600
18.70	506.826	21.60	861.404	24.50	1539.545
18.80	515.438	21.70	878.369	24.60	1571.132
18.90	524.260	21.80	895.719	24.70	1603.371
19.00	533.296	21.90	913.461	24.80	1636.275
19.10	542.553	22.00	931.602	24.90	1669.856
19.20	552.034	22.10	950.151	25.00	1704.124
Temperature = 383.15 K					
0.20	6.287	2.50	67.851	4.80	114.577
0.30	9.369	2.60	70.139	4.90	116.380
0.40	12.409	2.70	72.401	5.00	118.169
0.50	15.410	2.80	74.635	5.10	119.944
0.60	18.370	2.90	76.843	5.20	121.706
0.70	21.292	3.00	79.025	5.30	123.455
0.80	24.175	3.10	81.183	5.40	125.192
0.90	27.020	3.20	83.316	5.50	126.918
1.00	29.828	3.30	85.425	5.60	128.632
1.10	32.599	3.40	87.510	5.70	130.335
1.20	35.334	3.50	89.573	5.80	132.029
1.30	38.033	3.60	91.614	5.90	133.713
1.40	40.696	3.70	93.633	6.00	135.388
1.50	43.326	3.80	95.631	6.10	137.054
1.60	45.921	3.90	97.608	6.20	138.712
1.70	48.483	4.00	99.566	6.30	140.363
1.80	51.013	4.10	101.504	6.40	142.007
1.90	53.510	4.20	103.423	6.50	143.645
2.00	55.975	4.30	105.325	6.60	145.276
2.10	58.410	4.40	107.208	6.70	146.093
2.20	60.814	4.50	109.074	6.80	148.524
2.30	63.189	4.60	110.924	6.90	150.142
2.40	65.534	4.70	112.758	7.00	151.755

P-ρ-T Table for Carbon Dioxide

Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)
Temperature = 383.15 K (continued)					
7.10	153.365	12.40	250.372	17.70	478.539
7.20	154.973	12.50	252.811	17.80	485.935
7.30	156.578	12.60	255.292	17.90	493.505
7.40	158.182	12.70	257.815	18.00	501.253
7.50	159.785	12.80	260.382	18.10	509.182
7.60	161.387	12.90	262.995	18.20	517.297
7.70	162.989	13.00	265.655	18.30	525.602
7.80	164.592	13.10	268.362	18.40	534.102
7.90	166.196	13.20	271.119	18.50	542.801
8.00	167.802	13.30	273.928	18.60	551.704
8.10	169.409	13.40	276.789	18.70	560.815
8.20	171.020	13.50	279.704	18.80	570.139
8.30	172.634	13.60	282.676	18.90	579.681
8.40	174.252	13.70	285.705	19.00	589.446
8.50	175.875	13.80	288.793	19.10	599.439
8.60	177.502	13.90	291.941	19.20	609.665
8.70	179.136	14.00	295.153	19.30	620.128
8.80	180.776	14.10	298.429	19.40	630.835
8.90	182.423	14.20	301.771	19.50	641.791
9.00	184.077	14.30	305.181	19.60	653.000
9.10	185.740	14.40	308.662	19.70	664.469
9.20	187.412	14.50	312.214	19.80	676.202
9.30	189.094	14.60	315.841	19.90	688.207
9.40	190.786	14.70	319.544	20.00	700.487
9.50	192.489	14.80	323.324	20.10	713.050
9.60	194.203	14.90	327.186	20.20	725.900
9.70	195.931	15.00	331.130	20.30	739.045
9.80	197.671	15.10	335.159	20.40	752.489
9.90	199.425	15.20	339.275	20.50	766.240
10.00	201.194	15.30	343.480	20.60	780.303
10.10	202.979	15.40	347.778	20.70	794.685
10.20	204.780	15.50	352.171	20.80	809.393
10.30	206.598	15.60	356.660	20.90	824.432
10.40	208.434	15.70	361.249	21.00	839.809
10.50	210.288	15.80	365.941	21.10	855.532
10.60	212.163	15.90	370.737	21.20	871.607
10.70	214.058	16.00	375.642	21.30	888.041
10.80	215.974	16.10	380.657	21.40	904.840
10.90	217.913	16.20	685.786	21.50	922.013
11.00	219.875	16.30	391.032	21.60	939.566
11.10	221.862	16.40	396.397	21.70	957.507
11.20	223.873	16.50	401.885	21.80	975.843
11.30	225.911	16.60	407.499	21.90	994.582
11.40	227.977	16.70	413.242	22.00	1013.731
11.50	230.070	16.80	419.118	22.10	1033.299
11.60	232.193	16.90	425.129	22.20	1053.292
11.70	234.347	17.00	431.280	22.30	1073.720
11.80	236.532	17.10	437.574	22.40	1094.590
11.90	238.750	17.20	444.014	22.50	1115.911
12.00	241.002	17.30	450.604	22.60	1137.690
12.10	243.289	17.40	457.347	22.70	1159.938
12.20	245.612	17.50	464.249	22.80	1182.661
12.30	247.972	17.60	471.311	22.90	1205.870

P-ρ-T Table for Carbon Dioxide

Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)
Temperature = 383.15 K (continued)					
23.00	1229.572	23.70	1410.101	24.40	1618.624
23.10	1253.778	23.80	1438.094	24.50	1650.910
23.20	1278.495	23.90	1455.668	24.60	1683.853
23.30	1303.735	24.00	1495.833	24.70	1717.466
23.40	1329.505	24.10	1525.601	24.80	1751.761
23.50	1355.816	24.20	1555.981	24.90	1786.749
23.60	1382.678	24.30	1586.985	25.00	1822.442
Temperature = 393.15 K					
0.20	6.457	4.60	116.401	9.00	197.693
0.30	9.626	4.70	118.387	9.10	199.582
0.40	12.755	4.80	120.359	9.20	201.483
0.50	15.847	4.90	122.318	9.30	203.395
0.60	18.900	5.00	124.263	9.40	205.320
0.70	21.915	5.10	126.196	9.50	207.258
0.80	24.894	5.20	128.118	9.60	209.211
0.90	27.837	5.30	130.027	9.70	211.178
1.00	30.743	5.40	131.926	9.80	213.162
1.10	33.615	5.50	133.815	9.90	215.161
1.20	36.452	5.60	135.693	10.00	217.178
1.30	39.254	5.70	137.563	10.10	219.213
1.40	42.024	5.80	139.424	10.20	221.267
1.50	44.760	5.90	141.277	10.30	223.341
1.60	47.464	6.00	143.122	10.40	225.436
1.70	50.136	6.10	144.960	10.50	227.552
1.80	52.777	6.20	146.792	10.60	229.690
1.90	55.388	6.30	148.617	10.70	231.852
2.00	57.968	6.40	150.438	10.80	234.039
2.10	60.519	6.50	152.253	10.90	236.250
2.20	63.041	6.60	154.064	11.00	238.489
2.30	65.534	6.70	155.871	11.10	240.754
2.40	68.000	6.80	157.675	11.20	243.048
2.50	70.439	6.90	159.477	11.30	245.371
2.60	72.851	7.00	161.276	11.40	247.725
2.70	75.238	7.10	163.073	11.50	250.110
2.80	77.599	7.20	164.870	11.60	252.528
2.90	79.935	7.30	166.666	11.70	254.980
3.00	82.246	7.40	168.462	11.80	257.467
3.10	84.534	7.50	170.259	11.90	259.990
3.20	86.799	7.60	172.057	12.00	262.551
3.30	89.042	7.70	173.857	12.10	265.150
3.40	91.262	7.80	175.660	12.20	267.789
3.50	93.462	7.90	177.465	12.30	270.470
3.60	95.640	8.00	179.274	12.40	273.193
3.70	97.798	8.10	181.087	12.50	275.959
3.80	99.936	8.20	182.904	12.60	278.771
3.90	102.055	8.30	184.728	12.70	281.630
4.00	104.156	8.40	186.557	12.80	284.537
4.10	106.239	8.50	188.393	12.90	287.493
4.20	108.304	8.60	190.236	13.00	290.500
4.30	110.352	8.70	192.086	13.10	293.560
4.40	112.384	8.80	193.946	13.20	296.674
4.50	114.400	8.90	195.815	13.30	299.843

P-ρ-T Table for Carbon Dioxide

Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)
Temperature = 393.15 K (continued)					
13.40	303.069	17.30	495.371	21.20	945.622
13.50	306.355	17.40	502.714	21.30	962.983
13.60	309.700	17.50	510.222	21.40	980.720
13.70	313.108	17.60	517.899	21.50	998.841
13.80	316.580	17.70	525.748	21.60	1017.352
13.90	320.118	17.80	533.774	21.70	1036.262
14.00	323.723	17.90	541.980	21.80	1055.577
14.10	327.398	18.00	550.371	21.90	1075.306
14.20	331.144	18.10	558.950	22.00	1095.456
14.30	334.964	18.20	567.724	22.10	1116.036
14.40	338.858	18.30	576.695	22.20	1137.053
14.50	342.830	18.40	585.869	22.30	1158.516
14.60	346.882	18.50	595.249	22.40	1180.433
14.70	351.015	18.60	604.841	22.50	1202.812
14.80	355.232	18.70	614.649	22.60	1225.662
14.90	359.534	18.80	624.678	22.70	1248.922
15.00	363.925	18.90	634.933	22.80	1272.810
15.10	368.407	19.00	645.419	22.90	1297.127
15.20	372.981	19.10	656.141	23.00	1321.949
15.30	377.651	19.20	667.104	23.10	1347.288
15.40	382.419	19.30	678.313	23.20	1373.152
15.50	387.288	19.40	689.774	23.30	1399.551
15.60	392.259	19.50	701.491	23.40	1426.495
15.70	397.336	19.60	713.471	23.50	1453.994
15.80	402.522	19.70	725.719	23.60	1482.057
15.90	407.819	19.80	738.240	23.70	1510.695
16.00	413.230	19.90	751.041	23.80	1539.918
16.10	418.758	20.00	764.126	23.90	1569.737
16.20	424.406	20.10	777.503	24.00	1600.162
16.30	430.177	20.20	791.176	24.10	1631.204
16.40	436.075	20.30	805.153	24.20	1662.875
16.50	442.101	20.40	819.438	24.30	1695.186
16.60	448.261	20.50	834.039	24.40	1728.147
16.70	454.556	20.60	848.962	24.50	1761.772
16.80	460.990	20.70	864.213	24.60	1796.070
16.90	467.567	20.80	879.798	24.70	1831.055
17.00	474.290	20.90	895.725	24.80	1866.739
17.10	481.162	21.00	912.000	24.90	1903.133
17.20	488.188	21.10	928.630	25.00	1940.252
Temperature = 403.15 K					
0.20	6.627	1.50	46.189	2.80	80.544
0.30	9.883	1.60	49.000	2.90	83.007
0.40	13.101	1.70	51.782	3.00	85.447
0.50	16.283	1.80	54.534	3.10	87.864
0.60	19.428	1.90	57.256	3.20	90.260
0.70	22.537	2.00	59.591	3.30	92.635
0.80	25.612	2.10	62.617	3.40	94.989
0.90	28.651	2.20	65.255	3.50	97.324
1.00	31.656	2.30	67.867	3.60	99.638
1.10	34.628	2.40	70.453	3.70	101.934
1.20	37.566	2.50	73.013	3.80	104.212
1.30	40.472	2.60	75.548	3.90	106.471
1.40	43.346	2.70	78.058	4.00	108.714

P-ρ-T Table for Carbon Dioxide

Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)
Temperature = 403.15 K (continued)					
4.10	110.940	9.50	221.971	14.90	391.862
4.20	113.149	9.60	224.162	15.00	396.698
4.30	115.343	9.70	226.370	15.10	401.631
4.40	117.523	9.80	228.597	15.20	406.662
4.50	119.687	9.90	230.843	15.30	411.794
4.60	121.838	10.00	233.109	15.40	417.030
4.70	123.976	10.10	235.395	15.50	422.372
4.80	126.101	10.20	237.703	15.60	427.823
4.90	128.213	10.30	240.034	15.70	433.386
5.00	130.314	10.40	242.388	15.80	439.063
5.10	132.404	10.50	244.767	15.90	444.858
5.20	134.483	10.60	247.170	16.00	450.773
5.30	136.552	10.70	249.601	16.10	456.811
5.40	138.612	10.80	252.058	16.20	462.975
5.50	140.663	10.90	254.544	16.30	469.268
5.60	142.705	11.00	257.059	16.40	475.694
5.70	144.740	11.10	259.605	16.50	482.256
5.80	146.768	11.20	262.182	16.60	488.956
5.90	148.789	11.30	264.792	16.70	495.799
6.00	150.803	11.40	267.435	16.80	502.788
6.10	152.813	11.50	270.113	16.90	509.926
6.20	154.817	11.60	272.828	17.00	517.216
6.30	156.816	11.70	275.579	17.10	524.663
6.40	158.812	11.80	278.370	17.20	532.270
6.50	160.805	11.90	281.199	17.30	240.041
6.60	162.794	12.00	284.070	17.40	547.980
6.70	164.782	12.10	286.983	17.50	556.090
6.80	166.768	12.20	289.939	17.60	564.375
6.90	168.753	12.30	292.941	17.70	572.841
7.00	170.737	12.40	295.989	17.80	581.489
7.10	172.722	12.50	299.084	17.90	590.326
7.20	174.707	12.60	302.229	18.00	599.355
7.30	176.693	12.70	305.424	18.10	608.580
7.40	178.682	12.80	308.671	18.20	618.006
7.50	180.672	12.90	311.972	18.30	627.637
7.60	182.666	13.00	315.327	18.40	637.479
7.70	184.664	13.10	318.740	18.50	647.534
7.80	186.665	13.20	322.211	18.60	657.809
7.90	188.672	13.30	325.742	18.70	668.308
8.00	190.684	13.40	329.334	18.80	679.036
8.10	192.702	13.50	332.990	18.90	689.997
8.20	194.727	13.60	336.710	19.00	701.198
8.30	196.760	13.70	340.498	19.10	712.642
8.40	198.800	13.80	344.354	19.20	724.335
8.50	200.849	13.90	348.281	19.30	736.283
8.60	202.908	14.00	352.280	19.40	748.491
8.70	204.976	14.10	356.353	19.50	760.964
8.80	207.056	14.20	360.503	19.60	773.707
8.90	209.146	14.30	364.731	19.70	786.727
9.00	211.249	14.40	369.039	19.80	800.029
9.10	213.365	14.50	373.430	19.90	813.619
9.20	215.494	14.60	377.905	20.00	827.503
9.30	217.638	14.70	382.468	20.10	841.687
9.40	219.796	14.80	387.119	20.20	856.176



P-ρ-T Table for Carbon Dioxide

Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)
Temperature = 403.15 K (continued)					
20.30	870.997	21.90	1155.645	23.50	1551.718
20.40	886.097	22.00	1176.791	23.60	1580.979
20.50	901.541	22.10	1198.378	23.70	1610.830
20.60	917.316	22.20	1220.413	23.80	1641.281
20.70	933.429	22.30	1242.906	23.90	1672.342
20.80	949.886	22.40	1265.865	24.00	1704.025
20.90	966.695	22.50	1289.298	24.10	1736.340
21.00	983.861	22.60	1313.214	24.20	1769.300
21.10	1001.392	22.70	1337.622	24.30	1802.915
21.20	1019.294	22.80	1362.531	24.40	1837.198
21.30	1037.576	22.90	1387.951	24.50	1872.159
21.40	1056.245	23.00	1413.890	24.60	1907.812
21.50	1075.307	23.10	1440.359	24.70	1944.168
21.60	1094.770	23.20	1467.366	24.80	1981.239
21.70	1114.642	23.30	1494.921	24.90	2019.040
21.80	1134.931	23.40	1523.035	25.00	2057.581
Temperature = 413.15 K					
0.20	6.796	3.90	110.860	7.60	193.220
0.30	10.139	4.00	113.243	7.70	195.415
0.40	13.446	4.10	115.611	7.80	197.616
0.50	16.718	4.20	117.964	7.90	199.824
0.60	19.955	4.30	120.303	8.00	202.039
0.70	23.158	4.40	122.628	8.10	204.262
0.80	26.327	4.50	124.941	8.20	206.494
0.90	29.463	4.60	127.241	8.30	208.736
1.00	32.566	4.70	129.528	8.40	210.987
1.10	35.638	4.80	131.805	8.50	213.250
1.20	38.677	4.90	134.070	8.60	215.524
1.30	41.686	5.00	136.326	8.70	217.810
1.40	44.664	5.10	138.571	8.80	220.109
1.50	47.612	5.20	140.808	8.90	222.422
1.60	50.531	5.30	143.036	9.00	224.749
1.70	53.421	5.40	145.256	9.10	227.091
1.80	56.283	5.50	147.468	9.20	229.450
1.90	59.117	5.60	149.673	9.30	231.825
2.00	61.924	5.70	151.873	9.40	234.217
2.10	64.705	5.80	154.066	9.50	236.628
2.20	67.459	5.90	156.254	9.60	239.058
2.30	70.189	6.00	158.438	9.70	541.508
2.40	72.893	6.10	160.617	9.80	243.979
2.50	75.573	6.20	162.793	9.90	246.471
2.60	78.229	6.30	164.966	10.00	248.986
2.70	80.863	6.40	167.137	10.10	251.524
2.80	83.473	6.50	169.306	10.20	254.087
2.90	86.062	6.60	171.474	10.30	256.675
3.00	88.629	6.70	173.641	10.40	259.290
3.10	91.175	6.80	175.809	10.50	261.931
3.20	93.701	6.90	177.977	10.60	264.601
3.30	96.207	7.00	180.146	10.70	267.300
3.40	98.694	7.10	182.317	10.80	270.029
3.50	101.162	7.20	184.490	10.90	272.790
3.60	103.612	7.30	186.667	11.00	275.583
3.70	106.045	7.40	188.847	11.10	278.410
3.80	108.460	7.50	191.031	11.20	281.271

P-ρ-T Table for Carbon Dioxide

Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)
Temperature = 413.15 K (continued)					
11.30	284.168	15.90	481.831	20.50	968.747
11.40	287.102	16.00	488.247	20.60	985.369
11.50	290.074	16.10	494.791	20.70	1002.338
11.60	293.085	16.20	501.468	20.80	1019.661
11.70	296.137	16.30	508.281	20.90	1037.345
11.80	299.231	16.40	515.232	21.00	1055.396
11.90	302.368	16.50	522.325	21.10	1073.822
12.00	305.550	16.60	529.563	21.20	1092.631
12.10	308.777	16.70	536.950	21.30	1111.828
12.20	312.052	16.80	544.489	21.40	1131.422
12.30	315.375	16.90	552.184	21.50	1151.421
12.40	318.748	17.00	560.038	21.60	1171.831
12.50	322.173	17.10	568.056	21.70	1192.661
12.60	325.650	17.20	576.240	21.80	1213.919
12.70	329.182	17.30	584.594	21.90	1235.613
12.80	332.770	17.40	593.124	22.00	1257.750
12.90	336.416	17.50	601.831	22.10	1280.339
13.00	340.121	17.60	610.721	22.20	1303.389
13.10	343.887	17.70	619.798	22.30	1326.907
13.20	347.715	17.80	629.065	22.40	1350.903
13.30	351.607	17.90	638.527	22.50	1375.386
13.40	355.566	18.00	648.189	22.60	1400.365
13.50	359.592	18.10	658.054	22.70	1425.847
13.60	363.687	18.20	668.127	22.80	1451.844
13.70	637.854	18.30	678.413	22.90	1478.363
13.80	372.094	18.40	688.917	23.00	1505.416
13.90	376.409	18.50	699.642	23.10	1533.011
14.00	380.801	18.60	710.594	23.20	1561.157
14.10	385.273	18.70	721.778	23.30	1589.867
14.20	389.825	18.80	733.199	23.40	1619.148
14.30	394.461	18.90	744.861	23.50	1649.012
14.40	399.182	19.00	756.770	23.60	1679.470
14.50	403.991	19.10	768.931	23.70	1710.531
14.60	408.889	19.20	781.349	23.80	1742.207
14.70	413.880	19.30	794.030	23.90	1774.509
14.80	418.964	19.40	806.978	24.00	1807.447
14.90	424.145	19.50	820.200	24.10	1841.034
15.00	429.426	19.60	833.702	24.20	1875.281
15.10	434.808	19.70	847.488	24.30	1910.199
15.20	440.294	19.80	861.565	24.40	1945.801
15.30	445.886	19.90	875.938	24.50	1982.099
15.40	451.588	20.00	890.614	24.60	2019.104
15.50	457.402	20.10	905.598	24.70	2056.830
15.60	463.330	20.20	920.898	24.80	2095.289
15.70	469.376	20.30	936.518	24.90	2134.494
15.80	475.542	20.40	952.466	25.00	2174.459
Temperature = 423.15 K					
0.20	6.965	0.90	30.274	1.60	52.056
0.30	10.396	1.00	33.475	1.70	55.054
0.40	13.791	1.10	36.645	1.80	58.025
0.50	17.153	1.20	39.785	1.90	60.971
0.60	20.482	1.30	42.896	2.00	63.890
0.70	23.778	1.40	45.977	2.10	66.784
0.80	27.042	1.50	49.031	2.20	69.654

P-ρ-T Table for Carbon Dioxide

Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)
Temperature = 423.15 K (continued)					
2.30	72.500	7.70	206.116	13.10	368.988
2.40	75.322	7.80	208.516	13.20	373.173
2.50	78.121	7.90	210.924	13.30	377.427
2.60	80.899	8.00	213.342	13.40	381.751
2.70	83.654	8.10	215.770	13.50	386.147
2.80	86.388	8.20	218.209	13.60	390.617
2.90	89.101	8.30	220.660	13.70	395.163
3.00	91.795	8.40	223.123	13.80	399.786
3.10	94.469	8.50	225.598	13.90	404.489
3.20	97.124	8.60	228.088	14.00	409.274
3.30	99.760	8.70	230.591	14.10	414.143
3.40	102.379	8.80	233.110	14.20	419.097
3.50	104.980	8.90	235.645	14.30	424.139
3.60	107.564	9.00	238.197	14.40	429.272
3.70	110.133	9.10	240.766	14.50	434.497
3.80	112.685	9.20	243.353	14.60	439.817
3.90	115.223	9.30	245.960	14.70	445.234
4.00	117.746	9.40	248.586	14.80	450.750
4.10	120.255	9.50	251.233	14.90	456.368
4.20	122.751	9.60	253.902	15.00	462.091
4.30	125.234	9.70	256.594	15.10	467.920
4.40	127.705	9.80	259.308	15.20	473.859
4.50	130.164	9.90	262.048	15.30	479.910
4.60	132.612	10.00	264.812	15.40	486.075
4.70	135.049	10.10	267.602	15.50	492.358
4.80	137.476	10.20	270.420	15.60	498.761
4.90	139.894	10.30	273.265	15.70	505.288
5.00	142.303	10.40	276.140	15.80	511.940
5.10	144.704	10.50	279.045	15.90	518.721
5.20	147.096	10.60	281.981	16.00	525.635
5.30	149.482	10.70	284.949	16.10	532.683
5.40	151.861	10.80	287.950	16.20	539.870
5.50	154.234	10.90	290.986	16.30	547.198
5.60	156.602	11.00	294.057	16.40	554.671
5.70	158.965	11.10	297.165	16.50	562.292
5.80	161.323	11.20	300.311	16.60	570.065
5.90	163.678	11.30	303.495	16.70	577.993
6.00	166.030	11.40	306.720	16.80	586.079
6.10	168.379	11.50	309.986	16.90	594.327
6.20	170.726	11.60	313.295	17.00	602.741
6.30	173.072	11.70	316.648	17.10	611.325
6.40	175.417	11.80	320.046	17.20	620.082
6.50	177.762	11.90	323.490	17.30	629.016
6.60	180.108	12.00	326.983	17.40	638.131
6.70	182.454	12.10	330.525	17.50	647.432
6.80	184.802	12.20	334.118	17.60	656.922
6.90	187.153	12.30	337.763	17.70	666.606
7.00	189.506	12.40	341.462	17.80	676.487
7.10	191.864	12.50	345.216	17.90	686.570
7.20	194.225	12.60	349.027	18.00	696.860
7.30	196.591	12.70	352.896	18.10	707.360
7.40	198.962	12.80	356.825	18.20	718.076
7.50	201.340	12.90	360.815	18.30	729.012
7.60	203.724	13.00	364.869	18.40	740.173

P-ρ-T Table for Carbon Dioxide

Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)
Temperature = 423.15 K (continued)					
18.50	751.563	20.70	1070.945	22.90	1568.383
18.60	763.188	20.80	1089.129	23.00	1596.546
18.70	775.052	20.90	1107.683	23.10	1625.264
18.80	787.160	21.00	1126.615	23.20	1654.548
18.90	799.517	21.10	1145.932	23.30	1684.409
19.00	812.130	21.20	1165.640	23.40	1714.855
19.10	825.002	21.30	1185.749	23.50	1745.899
19.20	838.139	21.40	1206.264	23.60	1777.550
19.30	851.548	21.50	1227.195	23.70	1809.820
19.40	865.232	21.60	1248.548	23.80	1842.720
19.50	879.198	21.70	1270.331	23.90	1876.260
19.60	893.452	21.80	1292.553	24.00	1910.453
19.70	907.999	21.90	1315.222	24.10	1945.309
19.80	922.845	22.00	1338.347	24.20	1980.842
19.90	937.996	22.10	1361.934	24.30	2017.062
20.00	953.459	22.20	1385.994	24.40	2053.982
20.10	969.239	22.30	1410.535	24.50	2091.614
20.20	985.343	22.40	1435.565	24.60	2129.972
20.30	1001.777	22.50	1461.095	24.70	2169.066
20.40	1018.548	22.60	1487.132	24.80	2208.912
20.50	1035.662	22.70	1513.686	24.90	2249.522
20.60	1053.125	22.80	1540.766	25.00	2290.909
Temperature = 433.15 K					
0.20	7.135	3.20	100.530	6.20	178.620
0.30	10.652	3.30	103.296	6.30	181.138
0.40	14.136	3.40	106.045	6.40	183.657
0.50	17.588	3.50	108.779	6.50	186.177
0.60	21.008	3.60	111.497	6.60	188.700
0.70	24.397	3.70	114.200	6.70	191.225
0.80	27.755	3.80	116.889	6.80	193.754
0.90	31.083	3.90	119.564	6.90	196.286
1.00	34.381	4.00	122.227	7.00	198.824
1.10	37.650	4.10	124.876	7.10	201.366
1.20	40.890	4.20	127.514	7.20	203.915
1.30	44.103	4.30	130.140	7.30	206.470
1.40	47.287	4.40	132.755	7.40	209.033
1.50	50.445	4.50	135.360	7.50	211.603
1.60	53.577	4.60	137.955	7.60	214.182
1.70	56.682	4.70	140.541	7.70	216.771
1.80	59.762	4.80	143.118	7.80	219.369
1.90	62.817	4.90	145.687	7.90	221.978
2.00	65.848	5.00	148.249	8.00	224.599
2.10	68.856	5.10	150.804	8.10	227.231
2.20	71.840	5.20	153.352	8.20	229.877
2.30	74.802	5.30	155.895	8.30	232.536
2.40	77.741	5.40	158.433	8.40	235.210
2.50	80.659	5.50	160.966	8.50	237.898
2.60	83.556	5.60	163.495	8.60	240.603
2.70	86.433	5.70	166.021	8.70	243.324
2.80	89.290	5.80	168.544	8.80	246.062
2.90	92.127	5.90	171.064	8.90	248.819
3.00	94.946	6.00	173.584	9.00	251.595
3.10	97.747	6.10	176.102	9.10	254.391

P-ρ-T Table for Carbon Dioxide

Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)
Temperature = 433.15 K (continued)					
9.20	257.207	14.50	464.937	19.80	983.872
9.30	260.045	14.60	470.677	19.90	999.797
9.40	262.905	14.70	476.519	20.00	1016.042
9.50	265.789	14.80	482.465	20.10	1032.613
9.60	268.696	14.90	488.518	20.20	1049.517
9.70	271.629	15.00	494.681	20.30	1066.760
9.80	274.588	15.10	500.956	20.40	1084.349
9.90	277.573	15.20	507.345	20.50	1102.290
10.00	280.587	15.30	513.852	20.60	1120.591
10.10	283.629	15.40	520.479	20.70	1139.257
10.20	286.802	15.50	527.229	20.80	1158.297
10.30	289.805	15.60	534.105	20.90	1177.718
10.40	292.940	15.70	541.109	21.00	1197.526
10.50	296.108	15.80	548.245	21.10	1217.728
10.60	299.310	15.90	555.516	21.20	1238.333
10.70	302.547	16.00	562.924	21.30	1259.349
10.80	305.821	16.10	570.474	21.40	1280.781
10.90	309.131	16.20	578.168	21.50	1302.640
11.00	312.481	16.30	586.009	21.60	1324.931
11.10	315.870	16.40	594.001	21.70	1347.665
11.20	319.300	16.50	602.147	21.80	1370.848
11.30	322.772	16.60	610.450	21.90	1394.489
11.40	326.287	16.70	618.915	22.00	1418.597
11.50	329.847	16.80	627.545	22.10	1443.179
11.60	333.453	16.90	636.343	22.20	1468.246
11.70	337.107	17.00	645.313	22.30	1493.806
11.80	340.809	17.10	654.460	22.40	1519.867
11.90	344.561	17.20	663.786	22.50	1546.440
12.00	348.365	17.30	673.296	22.60	1573.533
12.10	352.221	17.40	682.994	22.70	1601.155
12.20	356.132	17.50	692.884	22.80	1629.317
12.30	360.099	17.60	702.970	22.90	1658.028
12.40	364.124	17.70	713.256	23.00	1687.299
12.50	368.207	17.80	723.747	23.10	1717.139
12.60	372.350	17.90	734.447	23.20	1747.558
12.70	376.556	18.00	745.360	23.30	1778.567
12.80	380.826	18.10	756.492	23.40	1810.177
12.90	385.161	18.20	767.846	23.50	1842.398
13.00	389.564	18.30	779.428	23.60	1875.241
13.10	394.035	18.40	791.241	23.70	1908.718
13.20	398.577	18.50	803.292	23.80	1942.839
13.30	403.192	18.60	815.584	23.90	1977.617
13.40	407.881	18.70	828.123	24.00	2013.062
13.50	412.646	18.80	840.915	24.10	2049.187
13.60	417.490	18.90	853.963	24.20	2086.004
13.70	422.414	19.00	867.274	24.30	2123.524
13.80	427.419	19.10	880.853	24.40	2161.762
13.90	432.509	19.20	894.705	24.50	2200.728
14.00	437.686	19.30	908.836	24.60	2240.436
14.10	442.950	19.40	923.251	24.70	2280.899
14.20	448.306	19.50	937.957	24.80	2322.131
14.30	453.754	19.60	952.958	24.90	2364.144
14.40	459.296	19.70	968.261	25.00	2406.952

P-ρ-T Table for Carbon Dioxide

Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)
Temperature = 443.15 K					
0.20	7.304	5.50	167.665	10.80	323.640
0.30	10.908	5.60	170.355	10.90	327.225
0.40	14.480	5.70	173.044	11.00	330.852
0.50	18.022	5.80	175.730	11.10	334.522
0.60	21.533	5.90	178.417	11.20	338.236
0.70	25.015	6.00	181.103	11.30	341.996
0.80	28.467	6.10	183.789	11.40	345.802
0.90	31.890	6.20	186.477	11.50	349.655
1.00	35.285	6.30	189.167	11.60	353.559
1.10	38.653	6.40	191.859	11.70	357.512
1.20	41.993	6.50	194.555	11.80	361.518
1.30	45.307	6.60	197.254	11.90	365.578
1.40	48.594	6.70	199.957	12.00	369.692
1.50	51.856	6.80	202.666	12.10	373.863
1.60	55.093	6.90	205.380	12.20	378.091
1.70	58.305	7.00	208.101	12.30	382.380
1.80	61.494	7.10	210.829	12.40	386.729
1.90	64.659	7.20	213.564	12.50	391.141
2.00	67.801	7.30	216.308	12.60	395.617
2.10	70.920	7.40	219.061	12.70	400.159
2.20	74.018	7.50	221.824	12.80	404.769
2.30	77.095	7.60	224.598	12.90	409.448
2.40	80.151	7.70	227.382	13.00	414.199
2.50	83.187	7.80	230.179	13.10	419.022
2.60	86.203	7.90	232.988	13.20	423.920
2.70	89.201	8.00	235.811	13.30	428.895
2.80	92.180	8.10	238.648	13.40	433.948
2.90	95.141	8.20	241.500	13.50	439.082
3.00	98.084	8.30	244.367	13.60	444.298
3.10	101.011	8.40	247.252	13.70	449.599
3.20	103.921	8.50	250.153	13.80	454.986
3.30	106.816	8.60	253.072	13.90	460.462
3.40	109.695	8.70	256.010	14.00	466.028
3.50	112.560	8.80	258.968	14.10	471.688
3.60	115.411	8.90	261.947	14.20	477.443
3.70	118.249	9.00	264.946	14.30	483.295
3.80	121.073	9.10	267.968	14.40	489.247
3.90	123.886	9.20	271.013	14.50	495.300
4.00	126.686	9.30	274.082	14.60	501.459
4.10	129.475	9.40	277.176	14.70	507.724
4.20	132.254	9.50	280.296	14.80	514.099
4.30	135.022	9.60	283.442	14.90	520.585
4.40	137.781	9.70	286.616	15.00	527.187
4.50	140.531	9.80	289.818	15.10	533.905
4.60	143.272	9.90	293.050	15.20	540.743
4.70	146.006	10.00	296.313	15.30	547.704
4.80	148.733	10.10	299.607	15.40	554.790
4.90	151.453	10.20	302.934	15.50	562.005
5.00	154.166	10.30	306.294	15.60	569.351
5.10	156.875	10.40	309.690	15.70	576.831
5.20	159.578	10.50	313.121	15.80	584.448
5.30	162.277	10.60	316.589	15.90	592.206
5.40	164.973	10.70	320.094	16.00	600.107

P-ρ-T Table for Carbon Dioxide

Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)
Temperature = 443.15 K (continued)					
16.10	608.155	19.10	936.485	22.10	1524.089
16.20	616.353	19.20	951.047	22.20	1550.159
16.30	624.704	19.30	965.897	22.30	1576.735
16.40	633.211	19.40	981.039	22.40	1603.825
16.50	641.879	19.50	996.479	22.50	1631.438
16.60	650.711	19.60	1012.223	22.60	1659.584
16.70	659.710	19.70	1028.278	22.70	1688.273
16.80	668.880	19.80	1044.650	22.80	1717.514
16.90	678.225	19.90	1061.343	22.90	1747.317
17.00	687.748	20.00	1078.366	23.00	1777.693
17.10	697.454	20.10	1095.724	23.10	1808.652
17.20	707.346	20.20	1113.424	23.20	1840.204
17.30	717.428	20.30	1131.472	23.30	1872.360
17.40	727.705	20.40	1149.875	23.40	1905.131
17.50	738.180	20.50	1168.640	23.50	1938.528
17.60	748.859	20.60	1187.773	23.60	1972.561
17.70	759.744	20.70	1207.283	23.70	2007.243
17.80	770.841	20.80	1227.175	23.80	2042.585
17.90	782.154	20.90	1247.458	23.90	2078.598
18.00	793.687	21.00	1268.138	24.00	2115.295
18.10	805.446	21.10	1289.223	24.10	2152.687
18.20	817.434	21.20	1310.721	24.20	2190.787
18.30	829.657	21.30	1332.639	24.30	2229.607
18.40	842.119	21.40	1354.986	24.40	2269.161
18.50	854.826	21.50	1377.768	24.50	2309.460
18.60	867.782	21.60	1400.995	24.60	2350.518
18.70	880.993	21.70	1424.675	24.70	2392.349
18.80	894.463	21.80	1448.816	24.80	2434.965
18.90	908.193	21.90	1473.426	24.90	2478.381
19.00	922.204	22.00	1498.514	25.00	2522.610
Temperature = 453.15 K					
0.20	7.473	2.40	82.553	4.60	148.567
0.30	11.164	2.50	85.706	4.70	151.448
0.40	14.824	2.60	88.841	4.80	154.323
0.50	18.456	2.70	91.059	4.90	157.193
0.60	22.058	2.80	95.059	5.00	160.058
0.70	25.632	2.90	98.142	5.10	162.919
0.80	29.178	3.00	101.210	5.20	165.777
0.90	32.697	3.10	104.262	5.30	168.632
1.00	36.188	3.20	107.299	5.40	171.485
1.10	39.654	3.30	110.322	5.50	174.336
1.20	43.094	3.40	113.331	5.60	177.186
1.30	46.508	3.50	116.327	5.70	180.036
1.40	49.898	3.60	119.310	5.80	182.886
1.50	53.263	3.70	122.281	5.90	185.737
1.60	56.605	3.80	125.240	6.00	188.590
1.70	59.924	3.90	128.188	6.10	191.444
1.80	63.220	4.00	131.126	6.20	194.302
1.90	66.494	4.10	134.054	6.30	197.163
2.00	69.747	4.20	136.973	6.40	200.028
2.10	72.978	4.30	139.883	6.50	202.898
2.20	76.190	4.40	142.785	6.60	205.773
2.30	79.381	4.50	145.679	6.70	208.654

P-ρ-T Table for Carbon Dioxide

Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)
Temperature = 453.15 K (continued)					
6.80	211.542	12.20	399.992	17.60	794.586
6.90	214.438	12.30	404.601	17.70	806.067
7.00	217.341	12.40	409.275	17.80	817.766
7.10	220.254	12.50	414.015	17.90	829.688
7.20	223.176	12.60	418.823	18.00	841.838
7.30	226.108	12.70	423.700	18.10	854.220
7.40	229.051	12.80	428.649	18.20	866.839
7.50	232.006	12.90	433.672	18.30	879.699
7.60	234.974	13.00	438.769	18.40	892.807
7.70	237.954	13.10	443.944	18.50	906.166
7.80	240.949	13.20	449.197	18.60	919.782
7.90	243.958	13.30	454.531	18.70	933.660
8.00	246.982	13.40	459.947	18.80	947.805
8.10	250.023	13.50	465.448	18.90	962.223
8.20	253.081	13.60	471.036	19.00	976.919
8.30	253.157	13.70	476.713	19.10	991.899
8.40	259.251	13.80	482.480	19.20	1007.168
8.50	262.364	13.90	488.341	19.30	1022.732
8.60	265.498	14.00	494.296	19.40	1038.597
8.70	268.653	14.10	500.349	19.50	1054.768
8.80	271.830	14.20	506.502	19.60	1071.252
8.90	275.030	14.30	512.757	19.70	1088.055
9.00	278.253	14.40	519.116	19.80	1105.183
9.10	281.501	14.50	525.582	19.90	1122.642
9.20	284.774	14.60	532.157	20.00	1140.439
9.30	288.074	14.70	538.844	20.10	1158.580
9.40	291.041	14.80	545.646	20.20	1177.071
9.50	294.756	14.90	552.564	20.30	1195.921
9.60	298.141	15.00	559.602	20.40	1215.134
9.70	301.556	15.10	566.762	20.50	1234.719
9.80	305.001	15.20	574.047	20.60	1254.682
9.90	308.479	15.30	581.459	20.70	1275.031
10.00	311.991	15.40	589.003	20.80	1295.772
10.10	215.536	15.50	596.680	20.90	1316.913
10.20	319.117	15.60	604.494	21.00	1338.462
10.30	322.735	15.70	612.447	21.10	1360.427
10.40	326.390	15.80	620.543	21.20	1382.814
10.50	330.083	15.90	628.785	21.30	1405.632
10.60	333.817	16.00	637.176	21.40	1428.889
10.70	337.591	16.10	645.720	21.50	1452.593
10.80	341.407	16.20	654.419	21.60	1476.752
10.90	345.267	16.30	663.277	21.70	1501.375
11.00	349.172	16.40	672.298	21.80	1526.470
11.10	353.122	16.50	681.485	21.90	1552.046
11.20	357.120	16.60	690.842	22.00	1578.112
11.30	361.166	16.70	700.372	22.10	1604.677
11.40	365.262	16.80	710.080	22.20	1631.749
11.50	369.409	16.90	719.968	22.30	1659.338
11.60	373.609	17.00	730.041	22.40	1687.453
11.70	377.863	17.10	740.303	22.50	1716.104
11.80	382.172	17.20	750.757	22.60	1745.301
11.90	386.538	17.30	761.409	22.70	1775.054
12.00	390.962	17.40	772.261	22.80	1805.372
12.10	395.446	17.50	783.319	22.90	1836.265



P-ρ-T Table for Carbon Dioxide

Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)
Temperature = 453.15 K (continued)					
23.00	1867.745	23.70	2105.415	24.40	2376.197
23.10	1899.821	23.80	2141.976	24.50	2417.829
23.20	1932.504	23.90	2179.223	24.60	2460.236
23.30	1965.806	24.00	2217.170	24.70	2503.433
23.40	1999.736	24.10	2255.828	24.80	2547.434
23.50	2034.307	24.20	2295.210	24.90	2592.252
23.60	2069.529	24.30	2335.329	25.00	2637.902
Temperature = 463.15 K					
0.20	7.642	4.70	156.867	9.20	298.492
0.30	11.419	4.80	159.890	9.30	302.022
0.40	15.168	4.90	162.910	9.40	305.582
0.50	18.889	5.00	165.926	9.50	309.172
0.60	22.582	5.10	168.939	9.60	312.795
0.70	26.248	5.20	171.951	9.70	316.450
0.80	29.888	5.30	174.961	9.80	320.138
0.90	33.502	5.40	177.971	9.90	323.862
1.00	37.090	5.50	180.980	10.00	327.622
1.10	40.653	5.60	183.990	10.10	331.418
1.20	44.192	5.70	187.001	10.20	335.253
1.30	47.707	5.80	190.014	10.30	339.127
1.40	51.199	5.90	193.029	10.40	343.041
1.50	54.668	6.00	196.047	10.50	346.996
1.60	58.114	6.10	199.069	10.60	350.995
1.70	61.539	6.20	202.096	10.70	355.037
1.80	64.942	6.30	205.127	10.80	359.124
1.90	68.325	6.40	208.165	10.90	363.258
2.00	71.688	6.50	211.208	11.00	367.440
2.10	75.031	6.60	214.259	11.10	371.670
2.20	78.355	6.70	217.318	11.20	375.951
2.30	81.660	6.80	220.385	11.30	380.283
2.40	84.948	6.90	223.461	11.40	384.668
2.50	88.218	7.00	226.547	11.50	389.108
2.60	91.471	7.10	229.644	11.60	393.604
2.70	94.707	7.20	232.752	11.70	398.157
2.80	97.928	7.30	235.872	11.80	402.768
2.90	101.134	7.40	239.005	11.90	407.440
3.00	104.325	7.50	242.152	12.00	412.174
3.10	107.502	7.60	245.313	12.10	416.971
3.20	110.665	7.70	248.489	12.20	421.833
3.30	113.815	7.80	251.681	12.30	426.762
3.40	116.953	7.90	254.889	12.40	431.759
3.50	120.079	8.00	258.115	12.50	436.826
3.60	123.193	8.10	261.359	12.60	441.965
3.70	126.297	8.20	264.623	12.70	447.177
3.80	129.391	8.30	267.906	12.80	452.465
3.90	132.475	8.40	271.210	12.90	457.830
4.00	135.549	8.50	274.535	13.00	463.273
4.10	138.616	8.60	277.883	13.10	468.798
4.20	141.674	8.70	281.255	13.20	474.405
4.30	144.725	8.80	284.650	13.30	480.097
4.40	147.769	8.90	288.071	13.40	485.875
4.50	150.807	9.00	291.517	13.50	491.743
4.60	153.840	9.10	294.991	13.60	497.701

P-ρ-T Table for Carbon Dioxide

Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)
Temperature = 463.15 K (continued)					
13.70	503.752	17.50	828.297	21.30	1478.338
13.80	509.899	17.60	840.150	21.40	1502.503
13.90	516.142	17.70	852.224	21.50	1527.126
14.00	522.486	17.80	864.522	21.60	1552.214
14.10	528.931	17.90	877.050	21.70	1577.778
14.20	535.480	18.00	889.813	21.80	1603.825
14.30	542.136	18.10	902.815	21.90	1630.365
14.40	548.901	18.20	916.061	22.00	1657.406
14.50	555.778	18.30	929.556	22.10	1684.957
14.60	562.768	18.40	943.305	22.20	1713.028
14.70	569.875	18.50	957.313	22.30	1741.628
14.80	577.101	18.60	971.586	22.40	1770.767
14.90	584.449	18.70	986.128	22.50	1800.455
15.00	591.921	18.80	1000.945	22.60	1830.700
15.10	599.521	18.90	1016.042	22.70	1861.515
15.20	607.251	19.00	1031.425	22.80	1892.907
15.30	615.114	19.10	1047.100	22.90	1924.889
15.40	623.112	19.20	1063.072	23.00	1957.471
15.50	631.250	19.30	1079.347	23.10	1990.662
15.60	639.529	19.40	1095.931	23.20	2024.475
15.70	647.954	19.50	1112.830	23.30	2058.920
15.80	656.526	19.60	1130.050	23.40	2094.008
15.90	665.250	19.70	1147.597	23.50	2129.752
16.00	674.129	19.80	1165.478	23.60	2166.162
16.10	683.166	19.90	1183.699	23.70	2203.250
16.20	692.364	20.00	1202.267	23.80	2241.028
16.30	701.727	20.10	1221.187	23.90	2279.509
16.40	711.258	20.20	1240.467	24.00	2318.704
16.50	720.962	20.30	1260.115	24.10	2358.627
16.60	730.841	20.40	1280.135	24.20	2399.291
16.70	740.899	20.50	1300.537	24.30	2440.707
16.80	751.141	20.60	1321.326	24.40	2482.890
16.90	761.570	20.70	1342.510	24.50	2525.852
17.00	772.190	20.80	1364.097	24.60	2569.608
17.10	783.005	20.90	1386.095	24.70	2614.171
17.20	794.019	21.00	1408.509	24.80	2659.555
17.30	805.236	21.10	1431.350	24.90	2705.775
17.40	816.661	21.20	1454.623	25.00	2752.844
Temperature = 473.15 K					
0.20	7.811	1.70	63.150	3.20	114.020
0.30	11.675	1.80	66.660	3.30	117.297
0.40	15.512	1.90	70.152	3.40	120.563
0.50	19.322	2.00	73.624	3.50	123.818
0.60	23.106	2.10	77.078	3.60	127.064
0.70	26.864	2.20	80.514	3.70	130.299
0.80	30.597	2.30	83.933	3.80	133.527
0.90	34.306	2.40	87.335	3.90	136.745
1.00	37.990	2.50	90.721	4.00	139.956
1.10	41.651	2.60	94.092	4.10	143.160
1.20	45.289	2.70	97.448	4.20	146.358
1.30	48.904	2.80	100.789	4.30	149.549
1.40	52.497	2.90	104.116	4.40	152.735
1.50	56.069	3.00	107.430	4.50	155.916
1.60	59.620	3.10	110.731	4.60	159.093

P-ρ-T Table for Carbon Dioxide

Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)
Temperature = 473.15 K (continued)					
4.70	162.267	10.10	347.254	15.50	665.712
4.80	165.437	10.20	351.341	15.60	674.455
4.90	168.605	10.30	355.471	15.70	683.348
5.00	171.772	10.40	359.644	15.80	692.395
5.10	174.937	10.50	363.861	15.90	701.599
5.20	178.102	10.60	368.124	16.00	710.963
5.30	181.267	10.70	372.433	16.10	720.490
5.40	184.432	10.80	376.791	16.20	730.185
5.50	187.599	10.90	381.198	16.30	740.050
5.60	190.768	11.00	385.656	16.40	750.090
5.70	193.940	11.10	390.165	16.50	760.307
5.80	197.115	11.20	394.728	16.60	770.706
5.90	200.294	11.30	399.346	16.70	781.290
6.00	203.477	11.40	404.020	16.80	792.064
6.10	206.666	11.50	408.752	16.90	803.030
6.20	209.861	11.60	413.543	17.00	814.194
6.30	213.063	11.70	418.394	17.10	825.560
6.40	216.272	11.80	423.307	17.20	837.130
6.50	219.489	11.90	428.284	17.30	848.911
6.60	222.715	12.00	433.327	17.40	860.905
6.70	225.950	12.10	438.436	17.50	873.118
6.80	229.196	12.20	443.614	17.60	885.553
6.90	232.452	12.30	448.861	17.70	898.216
7.00	235.721	12.40	454.181	17.80	911.110
7.10	239.001	12.50	459.574	17.90	924.242
7.20	242.295	12.60	465.043	18.00	937.614
7.30	245.603	12.70	470.589	18.10	951.233
7.40	248.925	12.80	476.214	18.20	965.103
7.50	252.263	12.90	481.920	18.30	979.230
7.60	255.617	13.00	487.708	18.40	993.617
7.70	258.988	13.10	493.582	18.50	1008.271
7.80	262.377	13.20	499.542	18.60	1023.197
7.90	265.784	13.30	505.591	18.70	1038.399
8.00	269.211	13.40	511.730	18.80	1053.885
8.10	272.658	13.50	517.963	18.90	1069.658
8.20	276.127	13.60	524.290	19.00	1085.725
8.30	279.617	13.70	530.715	19.10	1102.092
8.40	283.131	13.80	537.239	19.20	1118.763
8.50	286.668	13.90	543.864	19.30	1135.746
8.60	290.229	14.00	550.594	19.40	1153.046
8.70	293.816	14.10	557.430	19.50	1170.670
8.80	297.430	14.20	564.374	19.60	1188.623
8.90	301.071	14.30	571.430	19.70	1206.911
9.00	304.740	14.40	578.599	19.80	1225.542
9.10	308.439	14.50	585.885	19.90	1244.522
9.20	312.167	14.60	593.288	20.00	1263.857
9.30	315.927	14.70	600.814	20.10	1283.554
9.40	319.720	14.80	608.463	20.20	1303.620
9.50	323.545	14.90	616.239	20.30	1324.062
9.60	327.405	15.00	624.144	20.40	1344.887
9.70	331.299	15.10	632.181	20.50	1366.102
9.80	335.231	15.20	640.354	20.60	1387.714
9.90	339.199	15.30	648.664	20.70	1409.732
10.00	343.207	15.40	657.116	20.80	1432.162

P-ρ-T Table for Carbon Dioxide

Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)
Temperature = 473.15 K (continued)					
20.90	1455.012	22.30	1823.620	23.70	2300.763
21.00	1478.289	22.40	1853.781	23.80	2339.758
21.10	1502.003	22.50	1884.502	23.90	2379.471
21.20	1526.160	22.60	1915.795	24.00	2419.914
21.30	1550.770	22.70	1947.669	24.10	2461.101
21.40	1575.840	22.80	1980.135	24.20	2503.044
21.50	1601.378	22.90	2013.204	24.30	2545.757
21.60	1627.394	23.00	2046.885	24.40	2589.254
21.70	1653.896	23.10	2081.191	24.50	2633.546
21.80	1680.893	23.20	2116.131	24.60	2678.650
21.90	1708.393	23.30	2151.718	24.70	2724.578
22.00	1736.407	23.40	2187.963	24.80	2771.345
22.10	1764.943	23.50	2224.878	24.90	2818.965
22.20	1794.011	23.60	2262.474	25.00	2867.454
Temperature = 493.15 K					
0.20	8.149	4.00	148.727	7.80	283.668
0.30	12.186	4.10	152.205	7.90	287.473
0.40	16.199	4.20	155.679	8.00	291.300
0.50	20.187	4.30	159.149	8.10	295.152
0.60	24.152	4.40	162.617	8.20	299.029
0.70	28.094	4.50	166.083	8.30	302.933
0.80	32.014	4.60	169.547	8.40	306.864
0.90	35.911	4.70	173.011	8.50	310.822
1.00	39.787	4.80	176.475	8.60	314.810
1.10	43.643	4.90	179.939	8.70	318.827
1.20	47.477	5.00	183.404	8.80	322.876
1.30	51.292	5.10	186.871	8.90	326.956
1.40	55.088	5.20	190.341	9.00	331.069
1.50	58.864	5.30	193.813	9.10	335.217
1.60	62.622	5.40	197.289	9.20	339.399
1.70	66.363	5.50	200.770	9.30	343.617
1.80	70.086	5.60	204.256	9.40	347.872
1.90	73.793	5.70	207.747	9.50	352.166
2.00	77.483	5.80	211.245	9.60	356.498
2.10	81.157	5.90	214.750	9.70	360.871
2.20	84.817	6.00	218.262	9.80	365.286
2.30	88.462	6.10	221.784	9.90	369.743
2.40	92.092	6.20	225.314	10.00	374.244
2.50	95.710	6.30	228.855	10.10	378.790
2.60	99.314	6.40	232.406	10.20	383.382
2.70	102.906	6.50	235.968	10.30	383.022
2.80	106.486	6.60	239.543	10.40	392.710
2.90	110.055	6.70	243.130	10.50	397.448
3.00	113.613	6.80	246.732	10.60	402.238
3.10	117.161	6.90	250.347	10.70	407.080
3.20	120.699	7.00	253.978	10.80	411.976
3.30	124.228	7.10	257.625	10.90	416.927
3.40	127.749	7.20	261.289	11.00	421.935
3.50	131.262	7.30	264.970	11.10	427.001
3.60	134.767	7.40	268.669	11.20	432.127
3.70	138.266	7.50	272.388	11.30	437.313
3.80	141.759	7.60	276.127	11.40	442.562
3.90	145.245	7.70	279.887	11.50	447.875

P-ρ-T Table for Carbon Dioxide

Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)
Temperature = 493.15 K (continued)					
11.60	453.254	16.10	794.776	20.60	1519.762
11.70	458.699	16.20	805.457	20.70	1543.438
11.80	464.213	16.30	816.319	20.80	1567.546
11.90	469.798	16.40	827.368	20.90	1592.094
12.00	475.455	16.50	838.606	21.00	1617.090
12.10	481.185	16.60	850.037	21.10	1642.543
12.20	486.991	16.70	861.665	21.20	1668.461
12.30	492.874	16.80	873.495	21.30	1694.852
12.40	498.836	16.90	885.530	21.40	1721.725
12.50	504.879	17.00	897.774	21.50	1749.089
12.60	511.004	17.10	910.232	21.60	1776.952
12.70	517.214	17.20	922.908	21.70	1805.324
12.80	523.511	17.30	935.807	21.80	1834.214
12.90	529.895	17.40	948.932	21.90	1863.631
13.00	536.371	17.50	962.289	22.00	1893.584
13.10	542.938	17.60	975.882	22.10	1924.084
13.20	549.601	17.70	989.715	22.20	1955.140
13.30	556.360	17.80	1003.793	22.30	1986.762
13.40	563.217	17.90	1018.122	22.40	2018.960
13.50	570.176	18.00	1032.707	22.50	2051.744
13.60	577.238	18.10	1047.551	22.60	2085.126
13.70	584.405	18.20	1062.661	22.70	2119.115
13.80	591.680	18.30	1078.041	22.80	2153.722
13.90	599.065	18.40	1093.696	22.90	2188.959
14.00	606.563	18.50	1109.633	23.00	2224.836
14.10	614.176	18.60	1125.857	23.10	2261.365
14.20	621.906	18.70	1142.373	23.20	2298.558
14.30	629.757	18.80	1159.186	23.30	2336.425
14.40	637.729	18.90	1176.303	23.40	2374.979
14.50	645.827	19.00	1193.729	23.50	2414.233
14.60	654.053	19.10	1211.471	23.60	2454.197
14.70	662.410	19.20	1229.533	23.70	2494.885
14.80	670.900	19.30	1247.924	23.80	2536.310
14.90	679.526	19.40	1266.647	23.90	2578.484
15.00	688.292	19.50	1285.711	24.00	2621.420
15.10	697.199	19.60	1305.121	24.10	2665.131
15.20	706.252	19.70	1324.884	24.20	2709.632
15.30	715.453	19.80	1345.006	24.30	2754.936
15.40	724.805	19.90	1365.495	24.40	2801.056
15.50	734.311	20.00	1386.356	24.50	2848.007
15.60	743.975	20.10	1407.598	24.60	2895.804
15.70	753.800	20.20	1429.228	24.70	2944.460
15.80	763.789	20.30	1451.251	24.80	2993.990
15.90	773.946	20.40	1473.676	24.90	3044.411
16.00	784.273	20.50	1496.511	25.00	3095.736
Temperature = 513.15 K					
0.20	8.487	0.90	37.513	1.60	65.615
0.30	12.697	1.00	41.580	1.70	69.565
0.40	16.885	1.10	45.629	1.80	73.499
0.50	21.051	1.20	49.660	1.90	77.420
0.60	25.197	1.30	53.673	2.00	81.327
0.70	29.322	1.40	57.670	2.10	85.220
0.80	33.427	1.50	61.650	2.20	89.102

P-ρ-T Table for Carbon Dioxide

Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)
Temperature = 513.15 K (continued)					
2.30	92.971	7.70	300.664	13.10	592.013
2.40	96.828	7.80	304.837	13.20	599.373
2.50	100.675	7.90	309.035	13.30	606.837
2.60	104.512	8.00	313.262	13.40	614.407
2.70	108.338	8.10	317.517	13.50	622.087
2.80	112.155	8.20	321.801	13.60	629.878
2.90	115.964	8.30	326.116	13.70	637.783
3.00	119.764	8.40	330.461	13.80	645.803
3.10	123.557	8.50	334.840	13.90	653.942
3.20	127.343	8.60	339.251	14.00	662.203
3.30	131.123	8.70	343.697	14.10	670.587
3.40	134.896	8.80	348.178	14.20	679.097
3.50	138.665	8.90	352.696	14.30	687.735
3.60	142.428	9.00	357.251	14.40	696.506
3.70	146.188	9.10	361.548	14.50	705.410
3.80	149.944	9.20	366.479	14.60	714.452
3.90	153.697	9.30	371.153	14.70	723.633
4.00	157.448	9.40	375.869	14.80	732.958
4.10	161.197	9.50	380.628	14.90	742.428
4.20	164.945	9.60	385.431	15.00	752.046
4.30	168.693	9.70	390.280	15.10	761.817
4.40	172.440	9.80	395.175	15.20	771.742
4.50	176.189	9.90	400.119	15.30	781.826
4.60	179.939	10.00	405.111	15.40	792.070
4.70	183.691	10.10	410.153	15.50	802.480
4.80	187.446	10.20	415.247	15.60	813.057
4.90	191.204	10.30	420.394	15.70	823.805
5.00	194.966	10.40	425.595	15.80	834.729
5.10	198.733	10.50	430.852	15.90	845.830
5.20	202.505	10.60	436.165	16.00	857.114
5.30	206.283	10.70	441.537	16.10	868.583
5.40	210.068	10.80	446.968	16.20	880.242
5.50	213.860	10.90	452.461	16.30	892.093
5.60	217.660	11.00	458.016	16.40	904.142
5.70	221.470	11.10	463.635	16.50	916.392
5.80	225.288	11.20	469.320	16.60	928.846
5.90	229.117	11.30	475.071	16.70	941.510
6.00	232.957	11.40	480.892	16.80	954.386
6.10	236.809	11.50	486.783	16.90	967.480
6.20	240.673	11.60	492.746	17.00	980.796
6.30	244.550	11.70	498.782	17.10	994.338
6.40	248.442	11.80	504.894	17.20	1008.110
6.50	252.348	11.90	511.082	17.30	1022.117
6.60	256.269	12.00	517.349	17.40	1036.364
6.70	260.207	12.10	523.697	17.50	1050.855
6.80	264.162	12.20	530.127	17.60	1065.595
6.90	268.135	12.30	536.641	17.70	1080.589
7.00	272.127	12.40	543.241	17.80	1095.842
7.10	276.138	12.50	549.929	17.90	1111.358
7.20	280.170	12.60	556.707	18.00	1127.144
7.30	284.223	12.70	563.576	18.10	1143.204
7.40	288.298	12.80	570.540	18.20	1159.543
7.50	292.396	12.90	577.599	18.30	1176.167
7.60	296.518	13.00	584.756	18.40	1193.081

P-ρ-T Table for Carbon Dioxide

Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)
Temperature = 513.15 K (continued)					
18.50	1210.291	20.70	1676.224	22.90	2363.636
18.60	1227.802	20.80	1702.001	23.00	2401.704
18.70	1245.620	20.90	1728.239	23.10	2440.451
18.80	1263.752	21.00	1754.946	23.20	2479.890
18.90	1282.202	21.10	1782.130	23.30	2520.033
19.00	1300.978	21.20	1809.800	23.40	2560.892
19.10	1320.084	21.30	1837.964	23.50	2602.479
19.20	1339.527	21.40	1866.632	23.60	2644.808
19.30	1359.315	21.50	1895.814	23.70	2687.891
19.40	1379.452	21.60	1925.517	23.80	2731.741
19.50	1399.946	21.70	1955.751	23.90	2776.372
19.60	1420.803	21.80	1986.526	24.00	2821.797
19.70	1442.030	21.90	2017.852	24.10	2868.030
19.80	1463.634	22.00	2049.738	24.20	2915.085
19.90	1485.622	22.10	2082.195	24.30	2962.976
20.00	1508.001	22.20	2115.232	24.40	3011.717
20.10	1530.778	22.30	2148.860	24.50	3061.323
20.20	1553.961	22.40	2183.089	24.60	3111.810
20.30	1577.557	22.50	2217.931	24.70	3163.191
20.40	1601.573	22.60	2253.395	24.80	3215.483
20.50	1626.018	22.70	2289.493	24.90	3268.701
20.60	1650.899	22.80	2326.236	25.00	3322.860
Temperature = 533.15 K					
0.20	8.825	3.20	133.957	6.20	255.948
0.30	13.207	3.30	137.985	6.30	260.160
0.40	17.570	3.40	142.010	6.40	264.390
0.50	21.914	3.50	146.032	6.50	268.638
0.60	26.240	3.60	150.052	6.60	272.904
0.70	30.548	3.70	154.071	6.70	277.191
0.80	34.839	3.80	158.088	6.80	281.498
0.90	39.112	3.90	162.106	6.90	285.826
1.00	43.370	4.00	166.124	7.00	290.177
1.10	47.611	4.10	170.143	7.10	294.551
1.20	51.837	4.20	174.164	7.20	298.949
1.30	56.049	4.30	178.186	7.30	303.371
1.40	60.246	4.40	182.212	7.40	307.820
1.50	64.429	4.50	186.242	7.50	312.295
1.60	68.599	4.60	190.275	7.60	316.799
1.70	72.756	4.70	194.314	7.70	321.330
1.80	76.902	4.80	198.358	7.80	325.891
1.90	81.035	4.90	202.408	7.90	330.483
2.00	85.157	5.00	206.465	8.00	335.106
2.10	89.269	5.10	210.530	8.10	339.762
2.20	93.371	5.20	214.603	8.20	344.451
2.30	97.463	5.30	218.685	8.30	349.175
2.40	101.546	5.40	222.777	8.40	353.934
2.50	105.621	5.50	226.879	8.50	358.730
2.60	109.688	5.60	230.992	8.60	363.564
2.70	113.747	5.70	235.117	8.70	368.436
2.80	117.800	5.80	239.255	8.80	373.348
2.90	121.847	5.90	243.406	8.90	378.301
3.00	125.889	6.00	247.572	9.00	383.296
3.10	129.925	6.10	251.752	9.10	388.334

P-ρ-T Table for Carbon Dioxide

Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)
Temperature = 533.15 K (continued)					
9.20	393.416	14.50	764.641	19.80	1581.487
9.30	398.544	14.60	774.492	19.90	1604.966
9.40	403.719	14.70	784.492	20.00	1628.854
9.50	408.941	14.80	794.645	20.10	1653.158
9.60	414.213	14.90	804.952	20.20	1677.886
9.70	419.535	15.00	815.417	20.30	1703.046
9.80	424.909	15.10	826.044	20.40	1728.646
9.90	430.335	15.20	836.836	20.50	1754.693
10.00	435.816	15.30	847.795	20.60	1781.196
10.10	441.352	15.40	858.926	20.70	1808.163
10.20	445.945	15.50	870.231	20.80	1835.602
10.30	452.596	15.60	881.714	20.90	1863.522
10.40	458.307	15.70	893.379	21.00	1891.931
10.50	464.079	15.80	905.230	21.10	1920.839
10.60	469.913	15.90	917.269	21.20	1950.254
10.70	475.812	16.00	929.501	21.30	1980.185
10.80	481.775	16.10	941.929	21.40	2010.642
10.90	487.806	16.20	954.558	21.50	2041.633
11.00	493.905	16.30	967.390	21.60	2073.169
11.10	500.074	16.40	980.432	21.70	2105.260
11.20	506.315	16.50	993.685	21.80	2137.914
11.30	512.629	16.60	1007.155	21.90	2171.143
11.40	519.017	16.70	1020.845	22.00	2204.956
11.50	525.482	16.80	1034.761	22.10	2239.363
11.60	532.026	16.90	1048.906	22.20	2274.376
11.70	538.026	17.00	1063.284	22.30	2310.004
11.80	545.354	17.10	1077.901	22.40	2346.259
11.90	552.143	17.20	1092.761	22.50	2383.152
12.00	559.016	17.30	1107.868	22.60	2420.694
12.10	565.977	17.40	1123.228	22.70	2458.896
12.20	573.027	17.50	1138.845	22.80	2497.770
12.30	580.168	17.60	1154.724	22.90	2537.328
12.40	587.402	17.70	1170.870	23.00	2577.581
12.50	594.731	17.80	1187.288	23.10	2618.542
12.60	602.157	17.90	1203.984	23.20	2660.223
12.70	609.681	18.00	1220.962	23.30	2702.637
12.80	617.307	18.10	1238.229	23.40	2745.796
12.90	625.036	18.20	1255.788	23.50	2789.714
13.00	632.871	18.30	1273.647	23.60	2834.403
13.10	640.813	18.40	1291.811	23.70	2879.877
13.20	648.865	18.50	1310.285	23.80	2926.149
13.30	657.029	18.60	1329.075	23.90	2973.233
13.40	665.307	18.70	1348.188	24.00	3021.144
13.50	673.703	18.80	1367.628	24.10	3069.895
13.60	682.217	18.90	1387.403	24.20	3119.501
13.70	690.854	19.00	1407.519	24.30	3169.976
13.80	699.615	19.10	1427.981	24.40	3221.335
13.90	708.503	19.20	1448.797	24.50	3273.594
14.00	717.520	19.30	1469.973	24.60	3326.768
14.10	726.669	19.40	1491.515	24.70	3380.872
14.20	735.953	19.50	1513.431	24.80	3435.922
14.30	745.374	19.60	1535.726	24.90	3491.935
14.40	754.936	19.70	1558.410	25.00	3548.926



P-ρ-T Table for Carbon Dioxide

Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)
Temperature = 553.15 K					
0.20	9.162	5.60	244.258	11.00	529.612
0.30	13.717	5.70	248.698	11.10	536.327
0.40	18.255	5.80	253.153	11.20	543.120
0.50	22.777	5.90	257.625	11.30	549.993
0.60	27.282	6.00	262.114	11.40	556.946
0.70	31.773	6.10	266.621	11.50	563.982
0.80	36.248	6.20	271.147	11.60	571.102
0.90	40.709	6.30	275.693	11.70	578.309
1.00	45.156	6.40	280.259	11.80	585.604
1.10	49.590	6.50	284.847	11.90	592.988
1.20	54.011	6.60	289.457	12.00	600.465
1.30	58.149	6.70	294.090	12.10	608.035
1.40	62.816	6.80	298.747	12.20	615.701
1.50	67.201	6.90	303.429	12.30	623.465
1.60	71.576	7.00	308.137	12.40	631.328
1.70	75.940	7.10	312.872	12.50	639.294
1.80	80.294	7.20	317.634	12.60	647.363
1.90	84.640	7.30	322.425	12.70	655.539
2.00	88.976	7.40	327.245	12.80	663.823
2.10	93.305	7.50	332.096	12.90	672.217
2.20	97.626	7.60	336.979	13.00	680.724
2.30	101.940	7.70	341.893	13.10	689.346
2.40	106.248	7.80	346.842	13.20	698.086
2.50	110.549	7.90	351.824	13.30	706.945
2.60	114.846	8.00	356.842	13.40	715.927
2.70	119.137	8.10	361.897	13.50	725.033
2.80	123.425	8.20	366.989	13.60	734.267
2.90	127.708	8.30	372.120	13.70	743.630
3.00	131.989	8.40	377.291	13.80	753.126
3.10	136.267	8.50	382.502	13.90	762.757
3.20	140.544	8.60	387.756	14.00	772.526
3.30	144.819	8.70	393.052	14.10	782.435
3.40	149.094	8.80	398.393	14.20	792.487
3.50	153.368	8.90	403.779	14.30	802.686
3.60	157.643	9.00	409.211	14.40	813.034
3.70	161.919	9.10	414.691	14.50	823.534
3.80	166.197	9.20	420.220	14.60	834.188
3.90	170.478	9.30	425.800	14.70	845.001
4.00	174.761	9.40	431.431	14.80	855.975
4.10	179.049	9.50	437.114	14.90	867.114
4.20	183.340	9.60	442.851	15.00	878.420
4.30	187.637	9.70	448.644	15.10	889.897
4.40	191.939	9.80	454.494	15.20	901.548
4.50	196.248	9.90	460.401	15.30	913.377
4.60	200.563	10.00	466.367	15.40	925.387
4.70	204.886	10.10	472.395	15.50	937.582
4.80	209.218	10.20	478.484	15.60	949.965
4.90	213.559	10.30	484.637	15.70	962.540
5.00	217.909	10.40	490.855	15.80	975.311
5.10	222.270	10.50	497.139	15.90	988.281
5.20	226.643	10.60	503.492	16.00	1001.454
5.30	231.027	10.70	509.913	16.10	1014.835
5.40	235.424	10.80	516.406	16.20	1028.426
5.50	239.834	10.90	522.972	16.30	1042.233

P-ρ-T Table for Carbon Dioxide

Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)
Temperature = 553.15 K (continued)					
16.40	1056.260	19.30	1579.950	22.20	2432.651
16.50	1070.510	19.40	1602.890	22.30	2470.275
16.60	1084.988	19.50	1626.220	22.40	2508.551
16.70	1099.698	19.60	1649.947	22.50	2547.490
16.80	1114.645	19.70	1674.078	22.60	2587.105
16.90	1129.833	19.80	1698.622	22.70	2627.406
17.00	1145.268	19.90	1723.584	22.80	2668.407
17.10	1160.952	20.00	1748.974	22.90	2710.118
17.20	1176.892	20.10	1774.798	23.00	2752.553
17.30	1193.092	20.20	1801.065	23.10	2795.723
17.40	1209.557	20.30	1827.782	23.20	2839.643
17.50	1226.292	20.40	1854.958	23.30	2884.324
17.60	1243.302	20.50	1882.601	23.40	2929.780
17.70	1260.593	20.60	1920.719	23.50	2976.024
17.80	1278.169	20.70	1939.321	23.60	3023.070
17.90	1296.036	20.80	1968.415	23.70	3070.931
18.00	1314.199	20.90	1998.011	23.80	3119.622
18.10	1332.665	21.00	2028.116	23.90	3169.156
18.20	1351.438	21.10	2058.742	24.00	3219.549
18.30	1370.524	21.20	2089.895	24.10	3270.815
18.40	1389.929	21.30	2121.587	24.20	3322.969
18.50	1409.659	21.40	2153.826	24.30	3376.025
18.60	1429.721	21.50	2186.623	24.40	3430.000
18.70	1450.120	21.60	2219.986	24.50	3484.909
18.80	1470.862	21.70	2253.927	24.60	3540.767
18.90	1491.954	21.80	2288.455	24.70	3597.592
19.00	1513.402	21.90	2323.581	24.80	3655.398
19.10	1535.213	22.00	2359.315	24.90	3714.203
19.20	1557.393	22.10	2395.668	25.00	3774.024
Temperature = 573.15 K					
0.20	9.500	2.50	115.463	4.80	220.032
0.30	14.227	2.60	119.987	4.90	224.662
0.40	18.940	2.70	124.509	5.00	229.304
0.50	23.638	2.80	129.030	5.10	233.960
0.60	28.324	2.90	133.549	5.20	238.630
0.70	32.996	3.00	138.068	5.30	243.314
0.80	37.656	3.10	142.587	5.40	248.015
0.90	42.304	3.20	147.107	5.50	252.732
1.00	46.940	3.30	151.628	5.60	257.466
1.10	51.565	3.40	156.151	5.70	262.218
1.20	56.180	3.50	160.677	5.80	266.989
1.30	60.785	3.60	165.205	5.90	271.779
1.40	65.381	3.70	169.738	6.00	276.590
1.50	69.967	3.80	174.275	6.10	281.423
1.60	74.546	3.90	178.816	6.20	286.277
1.70	79.116	4.00	183.364	6.30	291.154
1.80	83.679	4.10	187.918	6.40	296.056
1.90	88.236	4.20	192.479	6.50	300.982
2.00	92.786	4.30	197.048	6.60	305.934
2.10	97.330	4.40	201.625	6.70	310.912
2.20	101.870	4.50	206.212	6.80	315.918
2.30	106.404	4.60	210.808	6.90	320.952
2.40	110.935	4.70	215.414	7.00	326.015

P-ρ-T Table for Carbon Dioxide

Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)	Density, ρ (mol/l)	Pressure, P (bar)
Temperature = 573.15 K (continued)					
7.10	331.109	12.50	683.628	17.90	1387.552
7.20	336.234	12.60	692.337	18.00	1406.894
7.30	341.391	12.70	701.160	18.10	1426.551
7.40	346.581	12.80	710.097	18.20	1446.530
7.50	351.806	12.90	719.152	18.30	1466.837
7.60	357.066	13.00	728.328	18.40	1487.477
7.70	362.362	13.10	737.626	18.50	1508.457
7.80	367.695	13.20	747.048	18.60	1529.783
7.90	373.067	13.30	756.599	18.70	1551.461
8.00	378.478	13.40	766.279	18.80	1573.498
8.10	383.930	13.50	776.091	18.90	1595.900
8.20	389.423	13.60	786.039	19.00	1618.674
8.30	394.959	13.70	796.125	19.10	1641.827
8.40	400.539	13.80	806.351	19.20	1665.365
8.50	406.164	13.90	816.720	19.30	1689.296
8.60	411.835	14.00	827.235	19.40	1713.627
8.70	417.553	14.10	837.899	19.50	1738.364
8.80	423.320	14.20	848.715	19.60	1763.516
8.90	429.137	14.30	859.686	19.70	1789.090
9.00	435.005	14.40	870.814	19.80	1815.093
9.10	440.925	14.50	882.103	19.90	1841.533
9.20	446.899	14.60	893.556	20.00	1868.418
9.30	452.927	14.70	905.177	20.10	1895.756
9.40	459.012	14.80	916.967	20.20	1923.555
9.50	465.154	14.90	928.931	20.30	1951.824
9.60	471.355	15.00	941.072	20.40	1980.570
9.70	477.616	15.10	953.394	20.50	2009.802
9.80	483.938	15.20	965.899	20.60	2039.530
9.90	490.324	15.30	978.592	20.70	2069.761
10.00	496.773	15.40	991.476	20.80	2100.504
10.10	503.289	15.50	1004.554	20.90	2131.770
10.20	509.872	15.60	1017.831	21.00	2163.566
10.30	516.524	15.70	1031.309	21.10	2195.903
10.40	523.246	15.80	1044.994	21.20	2228.790
10.50	530.040	15.90	1058.889	21.30	2262.237
10.60	536.907	16.00	1072.997	21.40	2296.253
10.70	543.850	16.10	1087.324	21.50	2330.849
10.80	550.869	16.20	1101.872	21.60	2366.035
10.90	557.966	16.30	1116.647	21.70	2401.821
11.00	565.144	16.40	1131.653	21.80	2438.218
11.10	572.403	16.50	1146.893	21.90	2475.237
11.20	579.745	16.60	1162.373	22.00	2512.887
11.30	587.173	16.70	1178.096	22.10	2551.181
11.40	594.687	16.80	1194.068	22.20	2590.130
11.50	602.291	16.90	1210.293	22.30	2629.745
11.60	609.985	17.00	1226.776	22.40	2670.037
11.70	617.771	17.10	1243.522	22.50	2711.019
11.80	625.652	17.20	1260.535	22.60	2752.702
11.90	633.629	17.30	1277.821	22.70	2795.099
12.00	641.705	17.40	1295.385	22.80	2838.221
12.10	649.880	17.50	1313.231	22.90	2882.083
12.20	658.159	17.60	1331.366	23.00	2926.695
12.30	666.541	17.70	1349.794	23.10	2972.072
12.40	675.030	17.80	1368.521	23.20	3018.226

**P-ρ-T Table for Carbon Dioxide**

<b>Density, ρ (mol/l)</b>	<b>Pressure, P (bar)</b>	<b>Density, ρ (mol/l)</b>	<b>Pressure, P (bar)</b>	<b>Density, ρ (mol/l)</b>	<b>Pressure, P (bar)</b>
<b>Temperature = 573.15 K (continued)</b>					
23.30	3065.170	23.90	3364.220	24.50	3695.348
23.40	3112.919	24.00	3417.092	24.60	3753.888
23.50	3161.486	24.10	3470.870	24.70	3813.431
23.60	3210.886	24.20	3525.569	24.80	3873.991
23.70	3261.131	24.30	3581.204	24.90	3935.587
23.80	3312.238	24.40	3637.792	25.00	3998.235

## SOLUBILITY PARAMETERS OF THE MOST COMMON FLUIDS FOR SUPERCRITICAL FLUID EXTRACTION AND CHROMATOGRAPHY

The following table provides the solubility parameters,  $\delta$ , for the most common fluids and modifiers used in supercritical fluid extraction and chromatography. The data presented in the first table are for carrier or solvent supercritical fluids at a reduced temperature,  $T_r$ , of 1.02 and a reduced pressure,  $P_r$ , of 2. These values were calculated with the equation of Lee and Kesler.<sup>1,2</sup> The data presented in the second table are for liquid solvents that are potential modifiers.<sup>3</sup>

The solubility parameter is defined as the square root of the cohesive energy density. The most common presentation of the solubility parameter is in units of  $\text{cal}^{1/2}\text{cm}^{-3/2}$ . Here, the cohesive energy is expressed per unit volume. A more modern format that is found in some of the literature after 1990 utilizes SI units derived from cohesive pressures. It is possible to convert between the two scales with the following equations:

$$\delta(\text{cal}^{1/2}\text{cm}^{-3/2}) = 0.48888 \times \delta(\text{MPa}^{1/2}) \quad (4.1)$$

$$\delta(\text{MPa}^{1/2}) = 2.0455 \times \delta(\text{cal}^{1/2}\text{cm}^{-3/2}) \quad (4.2)$$

Thus, as a rough guide, the solubility parameters expressed in the SI system of cohesive pressures are numerically approximately double the values expressed in the older system.

## REFERENCES

1. Lee, B.I. and Kesler, M.G., Generalized thermodynamic correlation based on 3-parameter corresponding states, *AIChE J.*, 21, 510, 1975.
2. Schoenmakers, P.J. and Vunk, L.G.M., *Advances in Chromatography*, Vol. 30, Giddings, J.C., Grushka, E., and Brown, P.R., Eds., Marcel Dekker, New York, 1989.
3. Barton, A., *CRC Handbook of Solubility and Cohesive Energy Parameters*, CRC Press, Boca Raton, FL, 1983.

## SOLUBILITY PARAMETERS OF SUPERCRITICAL FLUIDS

In this table, the solubility parameter (in  $\text{cal}^{1/2}\text{cm}^{-3/2}$ ) was obtained by the methods outlined in references 1 and 2, and the conversion to the pressure scale was done by applying Equation 4.2.

Solubility Parameters of Supercritical Fluids		
Supercritical Fluid	$\delta(\text{cal}^{1/2}\text{cm}^{-3/2})$	$\delta(\text{MPa}^{1/2})$
Carbon dioxide	7.5	15.3
Nitrous oxide	7.2	14.7
Sulfur hexafluoride	5.5	11.3
Ammonia	9.3	19.0
Xenon	6.1	12.5
Ethane	5.8	11.9
Propane	5.5	11.3
<i>n</i> -Butane	5.3	10.8
Diethyl ether	5.4	11.0

## SOLUBILITY PARAMETERS OF LIQUID SOLVENTS

In this table, we provide solubility parameters for some liquid solvents that can be used as modifiers in supercritical fluid extraction and chromatography. The solubility parameters (in  $\text{MPa}^{1/2}$ ) were obtained from reference 3, and those in  $\text{cal}^{1/2}\text{cm}^{-3/2}$  were obtained by application of Equation 4.1 for consistency. It should be noted that other tabulations exist in which these values are slightly different, since they were calculated from different measured data or models. Therefore, the reader is cautioned that these numbers are for trend analysis and separation design only. For other applications of cohesive parameter calculations, it may be more advisable to consult a specific compilation. This table should be used along with the table on modifier decomposition, since many of these liquids show chemical instability, especially in contact with active surfaces.

Solubility Parameters of Liquid Solvents		
Liquid	$\delta(\text{cal}^{1/2}\text{cm}^{-3/2})$	$\delta(\text{MPa}^{1/2})$
<i>n</i> -Pentane	7.0	14.4
<i>n</i> -Hexane	7.3	14.9
<i>n</i> -Heptane	7.5	15.3
Cyclohexane	8.2	16.8
Benzene	9.1	18.7
Toluene	8.9	18.3
Acetone	9.6	19.7
Methyl ethyl ketone	9.4	19.3
Chloroform	9.1	18.7
Dichloromethane	9.9	20.2
Trichloroethene	9.1	18.7
Methanol	14.5	29.7
Ethanol	12.8	26.2
Diethyl ether	7.5	15.4
Tetrahydrofuran	9.0	18.5
1,4-Dioxane	10	20.5
Water	23.5	48.0

## INSTABILITY OF MODIFIERS USED WITH SUPERCRITICAL FLUIDS

Liquid modifiers that are commonly used to increase the effective polarity of supercritical fluids such as carbon dioxide frequently have inherent chemical instabilities that must be considered when designing an analysis, or in the interpretation of results.<sup>1-3</sup> In many cases, such solvents are obtainable with stabilizers added to control the instability or to slow the reaction. Reactive solvents that do not have stabilizers must be used quickly or be given proper treatment. In either case, it is important to understand that the solvents (as they may be used in an analysis) are not necessarily pure materials. The reader is cautioned that many of the other fluids listed earlier in this section are thermally unstable; this table only treats chemical instabilities that are considerable at typical laboratory ambient temperature.

## REFERENCES

1. Sadek, P.C., *The HPLC Solvent Guide*, 2nd ed., Wiley Interscience, New York, 2002.
2. Bruno, T.J. and Straty, G.C., *J. Res. Natl. Bur. Stand. (U.S.)*, Thermophysical property measurement on chemically reacting systems — a case study, 91, 135, 1986.
3. Asche, W., Mobile phases for supercritical fluid chromatography, *Chromatographia*, 11, 411, 1978.

**Instability of Modifiers Used with Supercritical Fluids**

Solvent	Contaminants, Reaction Products	Stabilizers
<b>Ethers</b>		
Diethyl ether	Peroxides <sup>a</sup>	2–3% (v/v) ethanol <sup>b</sup> 1–10 ppm (mass/mass) BHT (1.5–3.5% ethanol) + (0.2–0.5% water) + (5–10 ppm (mass/mass) BHT)
Isopropyl ether	Peroxides <sup>a</sup>	0.01% (mass/mass) hydroquinone 5–100 ppm (mass/mass) BHT
1,4-Dioxane	Peroxides <sup>a</sup>	25–1500 ppm (mass/mass) BHT
Tetrahydrofuran	Peroxides <sup>a</sup>	25–250 PPM (mass/mass) BHT
<b>Chlorinated Alkanes</b>		
Chloroform	Hydrochloric acid, chlorine, phosgene (CCl <sub>2</sub> O)	0.5–1% (v/v) ethanol 50–150 ppm (mass/mass) amylene <sup>c</sup> Various ethanol amylene blends
Dichloromethane	Hydrochloric acid, chlorine, phosgene (CCl <sub>2</sub> O)	25 ppm (mass/mass) amylene 25 ppm (mass/mass) cyclohexene 400–600 ppm (mass/mass) methanol Various amylene methanol blends
<b>Alcohols</b>		
Ethanol	Water, numerous denaturants are commonly added	
Methanol	Water; formaldehyde (at elevated temperature)	
Acetone	Diacetone alcohol and higher oligomers	

*Note:* BHT = 2,6-di-*t*-butyl-*p*-cresol.

<sup>a</sup> The peroxide concentration that is usually considered hazardous is 250 ppm (mass/mass).

<sup>b</sup> Ethanol does not actually stabilize diethyl ether, and it is not a peroxide scavenger, although it was thought to be so in the past. It is still available in chromatographic solvents to preserve the utility of retention relationships and analytical methods.

<sup>c</sup> Amylene is a generic name for 2-methyl-2-butene.

## CHAPTER 5

# Electrophoresis

### CONTENTS

Separation Ranges of Polyacrylamide Gels

Preparation of Polyacrylamide Gels

Buffer Mixtures Commonly Used for Polyacrylamide Gel Electrophoresis

Proteins for Internal Standardization of Polyacrylamide Gel Electrophoresis

Chromogenic Stains for Gels

Fluorescent Stains for Gels



## SEPARATION RANGES OF POLYACRYLAMIDE GELS

The following table provides a rough guide to the separation ranges of polyacrylamide gels that have varying gel concentrations, T, expressed in percent, as a function of relative molecular mass.<sup>1</sup>

### REFERENCES

1. Andrews, A.T., *Electrophoresis: Theory Techniques and Biochemical and Clinical Applications*, 2nd ed., Oxford University Press, Oxford, 1986.

Separation Ranges of Polyacrylamide Gels	
T (Percent)	Optimum Relative Molecular Mass Range
3–5	Above 100,000
5–12	20,000–150,000
10–15	10,000–80,000
15+	Below 15,000

From Andrews, A.T., *Electrophoresis: Theory Techniques and Biochemical and Clinical Applications*, 2nd ed., Oxford University Press, Oxford, 1986. With permission.

## PREPARATION OF POLYACRYLAMIDE GELS

The following table provides in recipe format the typical proportions of reagents needed to prepare 100 ml of the starting material for polyacrylamide gels.<sup>1</sup> The factor T is the gel concentration and is related to the ability to separate a given relative molecular mass range. Typically, the tertiary aliphatic amines *N,N,N,N*-tetramethylethylenediamine (TEMED) or 3-dimethylaminopropionitrile (DMAPN) are used to catalyze the reaction. Note that gelation does not occur readily below T = 2.5%.

## REFERENCES

1. Andrews, A.T., *Electrophoresis: Theory Techniques and Biochemical and Clinical Applications*, 2nd ed., Oxford University Press, Oxford, 1986.

Preparation of Polyacrylamide Gels			
Constituent	Amounts Required for Gels With		
	T = 5%	T = 7.5%	T = 10%
Acrylamide	4.75 g	7.125 g	9.50 g
Biscrylamide	0.25 g	0.375 g	0.50 g
TEMED or DMAPN	0.05 ml	0.05 ml	0.05 ml
Ammonium persulfate	0.05 g	0.05 g	0.05 g

From Andrews, A.T., *Electrophoresis: Theory Techniques and Biochemical and Clinical Applications*, 2nd ed., Oxford University Press, Oxford, 1986. With permission.

## BUFFER MIXTURES COMMONLY USED FOR POLYACRYLAMIDE GEL ELECTROPHORESIS

The following table provides suggested buffers used for polyacrylamide gel electrophoresis. This list is by no means exhaustive; however, these buffers are the most common.<sup>1</sup>

### REFERENCES

1. Andrews, A.T., *Electrophoresis: Theory Techniques and Biochemical and Clinical Applications*, 2nd ed., Oxford University Press, Oxford, 1986.

**Buffer Mixtures Commonly Used for Polyacrylamide Gel Electrophoresis**

Approximate pH Range	Primary Buffer Constituent	pH Adjusted to the Desired Value With
2.4–6.0	0.1 M citric acid	1 M NaOH
2.8–3.8	0.05 M formic acid	1 M NaOH
4.0–5.5	0.05 M acetic acid	1 M NaOH or tris
5.2–7.0	0.05 M maleic acid	1 M NaOH or tris
6.0–8.0	0.05 M $\text{KH}_2\text{PO}_4$ or $\text{NaH}_2\text{PO}_4$	1 M NaOH
7.0–8.5	0.05 M Sodium diethyl-barbiturate (veronal)	1 M HCl
7.2–9.0	0.05 M Tris	1 M HCl or glycine
8.5–10.0	0.015 M $\text{Na}_2\text{B}_4\text{O}_7$	1 M HCl or NaOH
9.0–10.5	0.05 M glycine	1 M NaOH
9.0–11.0	0.025 M $\text{NaHCO}_3$	1 M NaOH

From Andrews, A.T., *Electrophoresis: Theory Techniques and Biochemical and Clinical Applications*, 2nd ed., Oxford University Press, Oxford, 1986. With permission.

## PROTEINS FOR INTERNAL STANDARDIZATION OF POLYACRYLAMIDE GEL ELECTROPHORESIS

The following table provides a list of proteins that may be used as internal standards, along with their isoelectric points, pI, in quantitative applications of polyacrylamide gel electrophoresis. These proteins may be used in isoelectric focusing or in SDS-PAGE. The isoelectric points are reported at 25°C.<sup>1</sup>

### REFERENCES

1. Andrews, A.T., *Electrophoresis: Theory Techniques and Biochemical and Clinical Applications*, 2nd ed., Oxford University Press, Oxford, 1986.

**Proteins for Internal Standardization of Polyacrylamide Gel  
Electrophoresis**

<b>Protein</b>	<b>Isoelectric Point (pI at 25°C)</b>	<b>Relative Molecular Mass</b>
Lysozyme	10.0	14,000
Cytochrome C (horse)	9.3	12,256
Chymotrypsinogen A (ox)	9.0	23,600
Ribonuclease A	8.9	13,500
Myoglobin (sperm whale)	8.2	17,500
Myoglobin (horse)	7.3	17,500
Erythroagglutinin (red kidney bean)	6.5	130,000
Insulin (beef)	5.7	11,466
β-Lactoglobulin B	5.3	36,552
β-Lactoglobulin A	5.1	36,724
Bovine serum albumin	5.1	67,000
Ovalbumin	4.7	45,000
Alkaline phosphatase (calf intestine)	4.4	140,000
α-Lactalbumin	4.3	14,146

From Andrews, A.T., *Electrophoresis: Theory Techniques and Biochemical and Clinical Applications*, 2nd ed., Oxford University Press, Oxford, 1986. With permission.

## CHROMOGENIC STAINS FOR GELS

The following table provides common stain reagents for use in electrophoresis gels.<sup>1</sup>

### REFERENCES

1. Melvin, M., *Electrophoresis (Analytical Chemistry by Open Learning)*, John Wiley & Sons, Chichester, 1987.

**Chromogenic Stains for Gels**

Types of Substance Stained	Staining Reagent	Comments
Amino acids, peptides, and proteins	Ninhydrin	Very sensitive stain for amino acids, either free or combined in polypeptides; used after paper electrophoresis
Proteins	Amido Black 10B	Binds to cationic groups on proteins; adsorbs onto cellulose, giving high background staining with paper and dehydration and shrinkage of polyacrylamide gels
	Coomassie Brilliant Blue	Binds to basic groups on proteins and also by nonpolar interactions; widely used stain
	Ponceau S (Ponceau Red)	Used routinely in clinical laboratories for cellulose acetate and starch gels; very rapid staining reaction that leaves a clear background
Glycoproteins	Alcian Blue	Stains the sugar moiety
Copper-containing proteins	Alizarin Blue S	Specifically indicates the presence of copper
Polynucleotides, including RNA and DNA	Acridine orange	Stained product can be assessed quantitatively
	Pyronine Y (or G)	Gives a permanent staining, so electrophoretogram can be stored for several weeks
Proteins, lipids, carbohydrates, polynucleotides	Stains–All	Wide applicability, as it forms characteristic colored products with many different types of molecule; low sensitivity

From Melvin, M., *Electrophoresis (Analytical Chemistry by Open Learning)*, John Wiley & Sons, Chichester, 1987. With permission.

## FLUORESCENT STAINS FOR GELS

The following table provides common fluorescent stain reagents for use in electrophoresis.<sup>1</sup> Note that these agents are typically applied in small amounts before electrophoresis. Other stains are available as proprietary materials; consult reviews on staining procedures for additional materials.<sup>2,3</sup>

### REFERENCES

1. Melvin, M., *Electrophoresis (Analytical Chemistry by Open Learning)*, John Wiley & Sons, Chichester, 1987.
2. Williams, L.R., Staining nucleic acids and proteins in electrophoresis gels, *Biotech. Histochem.*, 76, 127, 2001.
3. Allen, R. and Budowle, B., *Protein Staining and Identification Techniques*, BioTechniques Press, Westborough, MA, 1999.

Fluorescent Stains for Gels		
Types of Substance Stained	Staining Reagent	Comments
Proteins	Dansyl chloride	Reacts with amine groups
	1-Anilino-8-naphthalene sulphonic acid	Nonfluorescent, but gives fluorescent product
	Fluorescamine	Nonfluorescent, but gives fluorescent product
Polynucleotides, including RNA and DNA	Acridine orange	
Double-stranded polynucleotides	Ethidium bromide	Very sensitive; widely used with agarose gels

From Melvin, M., *Electrophoresis (Analytical Chemistry by Open Learning)*, John Wiley & Sons, Chichester, 1987. With permission.

## CHAPTER 6

# Electroanalytical Methods

### CONTENTS

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## DETECTION LIMITS FOR VARIOUS ELECTROCHEMICAL TECHNIQUES

The following table provides guidance in selection of electrochemical techniques by providing the relative sensitivities of various methods.<sup>1</sup> The limit of detection of lead, defined as the minimum detectable quantity (on a mole basis), is used as the basis of comparison.

### REFERENCES

1. Batley, G.E., *Trace Element Speciation: Analytical Methods and Problems*, CRC Press, Boca Raton, FL, 1989.

Detection Limits for Various Electrochemical Techniques	
Electrochemical Technique	Limit of Detection for Lead (Mole)
DC polarography (DME)	$2 \times 10^{-6}$
DC polarography (SMDE)	$1 \times 10^{-7}$
DP polarography (SMDE)	$1 \times 10^{-7}$
DP anodic stripping voltammetry (HMDE)	$2 \times 10^{-10}$
SW anodic stripping voltammetry (HMDE)	$1 \times 10^{-10}$
DC anodic stripping voltammetry (TMFE)	$5 \times 10^{-11}$
DP anodic stripping voltammetry (TMFE)	$1 \times 10^{-11}$
SW anodic stripping voltammetry (TMFE)	$5 \times 10^{-12}$

*Note:* DC = direct current; DP = differential pulse; SW = square wave; DME = dropping mercury electrode; SMDE = static mercury drop electrode; HMDE = hanging mercury drop electrode; TMFE = thin mercury film electrode.



## VALUES OF (2.3026 RT/F) (IN mV) AT DIFFERENT TEMPERATURES

The following table gives the variation of (2.3026 RT/F) (mV) with temperature (°C).<sup>1</sup> Electronic pH meters are voltmeters with scale divisions that are equivalent to the value of 2.3026 RT/F (in mV) per pH unit. Generally, a reproducibility of  $\pm 0.005$  pH unit is feasible when the pH meter is reproducible to 0.2 mV.

## REFERENCES

1. Shugar, G.J. and Dean, J.A., *The Chemist's Ready Reference Handbook*, McGraw-Hill Book Company, New York, 1990.

Values of (2.3026 RT/F) (in mV) at Different Temperatures			
T (°C)	2.3026 RT/F (mV)	T (°C)	2.3026 RT/F (mV)
0	54.199	50	64.120
5	55.191	55	65.112
10	56.183	60	66.104
15	57.175	65	67.096
18	57.770	70	68.088
20	58.167	75	69.080
25	59.159	80	70.073
30	60.152	85	71.065
35	61.144	90	72.057
38	61.739	95	73.049
40	62.136	100	74.041
45	63.128		

## POTENTIAL OF ZERO CHARGE ( $E^{\text{ecm}}$ ) FOR VARIOUS ELECTRODE MATERIALS IN AQUEOUS SOLUTIONS AT ROOM TEMPERATURE

The table below lists the potential of zero charge ( $E^{\text{ecm}}$ ) values (in volts) for various electrode materials in aqueous solutions at room temperature (25°C).<sup>1</sup> All values are with respect to the normal hydrogen electrode.

### REFERENCES

1. Parsons, R., *Handbook of Electrochemical Constants*, Butterworths, London, 1959.

**Potential of Zero Charge ( $E^{\text{ecm}}$ ) for Various Electrode Materials  
in Aqueous Solutions at Room Temperature**

Electrode	$E^{\text{ecm}}$ (V)	Solution Composition
Ag	+0.05	0.1 N $\text{KNO}_3$
Cd	-0.90	0.0001 N KCl
Ga	-0.60	1 N KCl + 0.1 N HCl
Hg	-0.192	Capillary inactive salts <sup>a</sup>
Ni	-0.06	0.001 N HCl
Pb	-0.69	0.001 N KCl
Platinized Pt	+0.11	1 N $\text{Na}_2\text{SO}_4$ + 0.1 N $\text{H}_2\text{SO}_4$
Smooth Pt	+0.27	1 N $\text{Na}_2\text{SO}_4$ + 0.1 N $\text{H}_2\text{SO}_4$
Oxidized Pt	(+0.4)–(0.1)	1 N $\text{Na}_2\text{SO}_4$ + 0.1 N $\text{H}_2\text{SO}_4$
Te	+0.61	1 N $\text{Na}_2\text{SO}_4$
Tl	-0.80	0.001 N KCl
Tl–Hg (sat'd)	-0.65	1 N KCl
Zn	-0.63	1 N $\text{Na}_2\text{SO}_4$
Graphite	-0.07	0.05 N KCl
Activated charcoal	(0.0)–(+0.2)	1 N $\text{Na}_2\text{SO}_4$ + 0.1 N $\text{H}_2\text{SO}_4$

<sup>a</sup> Any salt that is nonreactive with the capillary can be used.

sat'd = saturated.

## VARIATION OF REFERENCE ELECTRODE POTENTIALS WITH TEMPERATURE

The following table lists the potentials of various (0.1 *M* KCl calomel, saturated KCl calomel, and 1.0 *M* KCl Ag/AgCl) electrodes at different temperatures (in °C).<sup>1-3</sup> The values include the liquid-junction potential.

### REFERENCES

1. Bates, R.G. et al., pH standards of high acidity and high alkalinity and the practical scale of pH, *J. Res. Natl. Bur. Stand.*, 45, 418, 1950.
2. Bates, R.G. and Bower, V.E., Standard potential of the silver silver-chloride electrode from 0-degrees C to 95-degrees C and the thermodynamic properties of dilute hydrochloric acid solutions, *J. Res. Natl. Bur. Stand.*, 53, 283, 1954.
3. Shugar, G.J. and Dean, J.A., *The Chemist's Ready Reference Handbook*, McGraw-Hill Book Company, New York, 1990.

Variation of Reference Electrode Potentials with Temperature			
Temperature (°C)	0.1 <i>M</i> KCl Calomel	Saturated KCl Calomel	1.0 <i>M</i> KCl Ag/AgCl
0	0.3367	0.25918	0.23655
5			0.23413
10	0.3362	0.25387	0.23142
15	0.3361	0.2511	0.22857
20	0.3358	0.24775	0.22557
25	0.3356	0.24453	0.22234
30	0.3354	0.24118	0.21904
35	0.3351	0.2376	0.21565
38	0.3350	0.2355	
40	0.3345	0.23449	0.21208
45			0.20835
50	0.3315	0.22737	0.20449
55			0.20056
60	0.3248	0.2235	0.19649
70			0.18782
80		0.2083	0.1787
90			0.1695

## pH VALUES OF STANDARD SOLUTIONS USED IN THE CALIBRATION OF GLASS ELECTRODES

The following table gives the pH values of operational standard solutions recommended for the calibration of glass electrodes at 25 and 37°C.<sup>1</sup>

### REFERENCES

1. Hibbert, D.B. and James, A.M., *Dictionary of Electrochemistry*, 2nd ed., John Wiley & Sons, New York, 1984.

**pH Values of Standard Solutions Used in the Calibration of Glass Electrodes**

Standard Solution	pH at	
	25°C	37°C
0.1 mol/kg potassium tetroxalate	1.48	1.49
0.1 mol/dm <sup>3</sup> hydrochloric acid + 0.09 mol/dm <sup>3</sup> potassium chloride	2.07	2.08
0.05 mol/kg potassium hydrogen phthalate	4.005	4.022
0.10 mol/dm <sup>3</sup> acetic acid + 0.10 mol/dm <sup>3</sup> sodium acetate	4.644	4.647
0.10 mol/dm <sup>3</sup> acetic acid + 0.01 mol/dm <sup>3</sup> sodium acetate	4.713	4.722
0.02 mol/kg pipezazine phosphate	6.26	6.14
0.025 mol/kg disodium hydrogen phosphate + 0.025 mol/kg potassium dihydrogen phosphate	6.857	6.828
0.05 mol/kg tris(hydroxymethyl)methane hydrochloride + 0.01667 mol/kg tris(hydroxymethyl)methane	7.648	7.332
0.05 mol/kg disodium tetraborate (borax)	9.182	9.074
0.025 mol/kg sodium bicarbonate + 0.025 mol/kg sodium carbonate	9.995	9.889
Saturated calcium hydroxide	12.43	12.05

## TEMPERATURE VS. pH CORRELATION OF STANDARD SOLUTIONS USED FOR THE CALIBRATION OF ELECTRODES

The following table gives the temperature vs. pH correlation of common standard solutions that are used for the calibration of electrodes.<sup>1-3</sup> Such solutions should be stable and easily prepared — solutions whose solutes do not require further purification because of factors such as their hygroscopic nature. It is worth noting that the buffering capacity of these solutions is of little interest.

### REFERENCES

1. Hibbert, D.B. and James, A.M., *Dictionary of Electrochemistry*, 2nd ed., John Wiley & Sons, New York, 1984.
2. Koryta, J., Dvůrák, J., and Bohácková, V., *Electrochemistry*, Methuen and Co., London, 1970.
3. Robinson, R.A. and Stokes, R.H., *Electrolytic Solutions*, Butterworths, London, 1959.

**Temperature vs. pH Correlation of Standard Solutions Used for the Calibration of Electrodes**

Temperature °C	pH of						
	0.05 M	Potassium	0.01 M	0.05 M	0.025 M		
	Potassium	Hydrogen	Potassium	Potassium	K <sub>2</sub> HPO <sub>4</sub> + 0.02 M	0.01 M	Ca(OH) <sub>2</sub> <sup>a</sup>
	Tetroxalate	Tartrate <sup>a</sup>	Tartrate	Hydrogen Phthalate	NaH <sub>2</sub> PO <sub>4</sub>	Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	
0	1.671	—	3.710	4.012	6.893	9.463	13.428
5	1.671	—	3.690	4.005	6.950	9.389	13.208
10	1.669	—	3.671	4.001	6.922	9.328	13.004
15	1.674	—	3.655	4.000	6.896	9.273	12.809
20	1.676	—	3.647	4.001	6.878	9.223	12.629
25	1.681	3.555	3.637	4.005	6.860	9.177	12.454
30	1.685	3.547	3.633	4.011	6.849	9.135	12.296
35	1.693	3.545	3.629	4.019	6.842	9.100	12.135
37	—	—	—	4.022	6.838	9.074	12.05
40	1.697	3.543	3.630	4.030	6.837	9.066	11.985
45	1.704	3.545	3.634	4.043	6.834	9.037	11.841
50	1.712	3.549	3.640	4.059	6.833	9.012	11.704
55	1.719	3.556	3.646	4.077	6.836	8.987	11.575
60	1.726	3.565	3.654	4.097	6.840	8.961	11.454
70	1.74	3.58	—	4.12	6.85	8.93	—
80	1.77	3.61	—	4.16	6.86	8.89	—
90	1.80	3.65	—	4.20	6.88	8.85	—
95	1.81	3.68	—	4.23	6.89	8.83	—

<sup>a</sup> Saturated at 25°C.

## SOLID MEMBRANE ELECTRODES

The following table lists the most commonly used solid membrane electrodes, their applications, and major interferences.<sup>1</sup> Often the membrane is composed of a salt (listed first) and a matrix (listed second). Thus, a AgCl–Ag<sub>2</sub>S electrode involves the finely divided AgCl in a Ag<sub>2</sub>S matrix. The salt should be more soluble than the matrix, but insoluble enough so that its equilibrium solubility gives a lower anion (Cl<sup>–</sup>) activity than that of the sample solution.

## REFERENCES

1. Fritz, J.S. and Schenk, G.H., *Quantitative Analytical Chemistry*, 5th ed., Prentice Hall, Englewood Cliffs, NJ, 1987.

Solid Membrane Electrodes		
Membrane	Ion Measured	Major Interferences
LaF <sub>3</sub>	F <sup>–</sup>	OH <sup>–</sup>
Ag <sub>2</sub> S	S <sup>2–</sup> , Ag <sup>+</sup>	Hg <sup>+2</sup>
AgCl–Ag <sub>2</sub> S	Cl <sup>–</sup>	Br <sup>–</sup> , I <sup>–</sup> , S <sup>2–</sup> , CN <sup>–</sup> , NH <sub>3</sub>
AgBr–Ag <sub>2</sub> S	Br <sup>–</sup>	I <sup>–</sup> , S <sup>2–</sup> , CN <sup>–</sup> , NH <sub>3</sub>
AgI–Ag <sub>2</sub> S	I <sup>–</sup>	S <sup>2–</sup> , CN <sup>–</sup>
AgSCN–Ag <sub>2</sub> S	SCN <sup>–</sup>	Br <sup>–</sup> , I <sup>–</sup> , S <sup>2–</sup> , CN <sup>–</sup> , NH <sub>3</sub>
CdS–Ag <sub>2</sub> S	Cd <sup>+2</sup>	Ag <sup>+</sup> , Hg <sup>+2</sup> , Cu <sup>+2</sup>
CuS–Ag <sub>2</sub> S	Cu <sup>+2</sup>	Ag <sup>+</sup> , Hg <sup>+2</sup>
PbS–Ag <sub>2</sub> S	Pb <sup>+2</sup>	Ag <sup>+</sup> , Hg <sup>+2</sup> , Cu <sup>+2</sup>

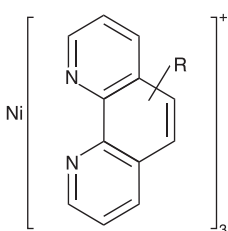
## LIQUID MEMBRANE ELECTRODES

The following table gives the basic information on several liquid membrane electrodes.<sup>1-3</sup> The selectivity of a membrane electrode for a given ion is determined primarily by the liquid ion exchanger used. Thus, as the preference of the ion exchanger for a specific ion increases, its selectivity increases. The selectivity is also affected by the organic solvent in which the liquid exchanger is dissolved. In this table, R- may be any organic radical or group.

## REFERENCES

1. Durst, R.A., Ed., *Ion-Selective Electrodes*, National Bureau of Standards Special Publication 314, Washington, D.C., 1969, p. 70.
2. Frant, M.S. and Ross, J.W., Potassium ion specific electrode with high selectivity for potassium over sodium, *Science*, 167, 987, 1970.
3. Fritz, J.S. and Schenk, G.H., *Quantitative Analytical Chemistry*, 5th ed., Prentice Hall, Englewood Cliffs, NJ, 1987.

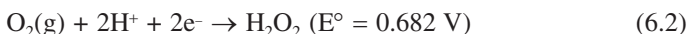
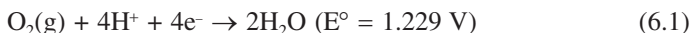
**Liquid Membrane Electrodes**

Ion Measured	Exchange Site	Selectivity Coefficients
K <sup>+</sup>	Valinomycin	Na <sup>+</sup> , 0.0001
Ca <sup>+2</sup>	(RO) <sub>2</sub> POO <sup>-</sup>	Na <sup>+</sup> , 0.0016 Mg <sup>+2</sup> , Ba <sup>+2</sup> , 0.01 Sr <sup>+2</sup> , 0.02 Zn <sup>+2</sup> , 3.2 H <sup>+</sup> , 10 <sup>7</sup>
Ca <sup>+2</sup> and Mg <sup>+2</sup>	(RO) <sub>2</sub> POO <sup>-</sup>	Na <sup>+</sup> , 0.01 Sr <sup>+2</sup> , 0.54 Ba <sup>+2</sup> , 0.94
Cu <sup>+2</sup>	RSCH <sub>2</sub> COO <sup>-</sup>	Na <sup>+</sup> , K <sup>+</sup> , 0.0005 Mg <sup>+2</sup> , 0.001 Ca <sup>+2</sup> , 0.002 Ni <sup>+2</sup> , 0.01 Zn <sup>+2</sup> , 0.03
NO <sub>3</sub> <sup>-</sup>		F <sup>-</sup> , 0.0009 SO <sub>4</sub> <sup>-2</sup> , 0.0006 PO <sub>4</sub> <sup>-3</sup> , 0.0003 Cl <sup>-</sup> , CH <sub>3</sub> COO <sup>-</sup> , 0.006 HCO <sub>3</sub> <sup>-</sup> , CN <sup>-</sup> , 0.02 NO <sub>2</sub> <sup>-</sup> , 0.06 Br <sup>-</sup> , 0.9
ClO <sub>4</sub> <sup>-</sup>		Cl <sup>-</sup> , SO <sub>4</sub> <sup>-2</sup> , 0.0002 Br <sup>-</sup> , 0.0006 NO <sub>3</sub> <sup>-</sup> , 0.0015 I <sup>-</sup> , 0.012 OH <sup>-</sup> , 1.0

## STANDARD REDUCTION ELECTRODE POTENTIALS FOR INORGANIC SYSTEMS IN AQUEOUS SOLUTIONS AT 25°C

A summary of the potentials,  $E^\circ$ , in volts (at 25°C), of the most useful reduction half reactions is presented below.<sup>1-5</sup> The reactions are arranged in order of decreasing oxidation strength. When comparing two half reactions, the oxidizing agent of the half reaction with the higher (more positive)  $E^\circ$  will react with the reducing agent of the half reaction with its lower (less positive)  $E^\circ$ . Thus,  $\text{Br}_2$  (l) ( $E^\circ = 1.065$  V) will oxidize  $\text{H}_2\text{O}_2$  to  $\text{O}_2$ (g) ( $E^\circ = 0.682$  V), but  $\text{O}_2$ (g) cannot oxidize  $\text{Br}^-$ . No predictions can be made on the rate of reaction.

If two or more reactions between two substances are possible, the reaction that involves half reactions that are farthest apart in the table will be most thermodynamically favorable. For instance, in the case of  $\text{O}_2$ (g) reacting with Cu,



The reaction between Equation 6.1 and Equation 6.3 will be most favorable. However, if Equation 6.3 is replaced with Equation 6.4,



the reactions between Equation 6.2 and Equation 6.4 will take place first.

## REFERENCES

1. Bard, A.J. and Faulkner, L.R., *Electrochemical Methods*, 2nd ed., John Wiley & Sons, New York, 2001.
2. Day, R.A. and Underwood, A.L., *Quantitative Analysis*, 6th ed., Prentice Hall, Englewood Cliffs, NJ, 1991.
3. Dean, J.A., Ed., *Lange's Handbook of Chemistry*, 14th ed., McGraw-Hill Book Co., New York, 1999.
4. Ebbing, D.D., *General Chemistry*, 6th ed., Houghton Mifflin Co., Boston, 1999.
5. Shugar, G.J. and Dean, J.A., *The Chemist's Ready Reference Handbook*, McGraw-Hill Book Co., New York, 1990.



**Standard Reduction Electrode Potentials for Inorganic  
Systems in Aqueous Solutions at 25°C**

Half Reaction		E°, V
$F_2(g) + 2H^+ + 2e^- \Rightarrow 2HF$		3.06
$O_3 + 2H^+ + 2e^- \Rightarrow O_2 + H_2O$		2.07
$S_2O_8^{2-} + 2e^- \Rightarrow 2SO_4^{2-}$		2.01
$Ag^{2+} + e^- \Rightarrow Ag^+$		2.00
$H_2O_2 + 2H^+ + 2e^- \Rightarrow 2H_2O$		1.77
$MnO_4^- + 4H^+ + 3e^- \Rightarrow MnO_2(s) + 2H_2O$		1.70
$Ce(IV) + e^- \Rightarrow Ce(III) \text{ (in } 1 \text{ M } HClO_4)$		1.61
$H_5IO_6 + H^+ + 2e^- \Rightarrow IO_3^- + 3H_2O$		1.6
$Bi_2O_4 + 4H^+ + 2e^- \Rightarrow 2BiO^+ + 2H_2O$		1.59
$BrO_3^- + 6H^+ + 5e^- \Rightarrow \frac{1}{2}Br_2 + 3H_2O$		1.52
$MnO_4^- + 8H^+ + 5e^- \Rightarrow Mn^{2+} + 4H_2O$		1.51
$PbO_2 + 4H^+ + 2e^- \Rightarrow Pb^{2+} + 2H_2O$		1.455
$Cl_2 + 2e^- \Rightarrow 2Cl^-$		1.36
$Cr_2O_7^{2-} + 14H^+ + 6e^- \Rightarrow 2Cr^{3+} + 7H_2O$		1.33
$MnO_2(s) + 4H^+ + 2e^- \Rightarrow Mn^{2+} + 2H_2O$		1.23
$O_2(g) + 4H^+ + 4e^- \Rightarrow 2H_2O$		1.229
$IO_3^- + 6H^+ + 5e^- \Rightarrow \frac{1}{2}I_2 + 3H_2O$		1.20
$Br_2(liq) + 2e^- \Rightarrow 2Br^-$		1.065
$ICl_2^- + e^- \Rightarrow \frac{1}{2}I_2 + 2Cl^-$		1.06
$VO_2^+ + 2H^+ + e^- \Rightarrow VO^{2+} + H_2O$		1.00
$HNO_2 + H^+ + e^- \Rightarrow NO(g) + H_2O$		1.00
$NO_3^- + 3H^+ + 2e^- \Rightarrow HNO_2 + H_2O$		0.94
$2Hg^{2+} + 2e^- \Rightarrow Hg_2^{2+}$		0.92
$Cu^{2+} + I^- + e^- \Rightarrow CuI$		0.86
$Ag^+ + e^- \Rightarrow Ag$		0.799
$Hg_2^{2+} + 2e^- \Rightarrow 2Hg$		0.79
$Fe^{3+} + e^- \Rightarrow Fe^{2+}$		0.771
$O_2(g) + 2H^+ + 2e^- \Rightarrow H_2O_2$		0.682
$2HgCl_2 + 2e^- \Rightarrow Hg_2Cl_2(s) + 2Cl^-$		0.63
$Hg_2SO_4(s) + 2e^- \Rightarrow 2Hg + SO_4^{2-}$		0.615
$H_3AsO_4 + 2H^+ + 2e^- \Rightarrow HAsO_2 + 2H_2O$		0.581
$Sb_2O_5 + 6H^+ + 4e^- \Rightarrow 2SbO^+ + 3H_2O$		0.559
$I_3^- + 2e^- \Rightarrow 3I^-$		0.545
$Cu^+ + e^- \Rightarrow Cu$		0.52
$VO^{2+} + 2H^+ + e^- \Rightarrow V^{3+} + H_2O$		0.361
$Fe(CN)_6^{3-} + e^- \Rightarrow Fe(CN)_6^{4-}$		0.36
$Cu^{2+} + 2e^- \Rightarrow Cu$		0.337
$UO_2^{2+} + 4H^+ + 2e^- \Rightarrow U^{4+} + 2H_2O$		0.334
$BiO^+ + 2H^+ + 3e^- \Rightarrow Bi + H_2O$		0.32
$Hg_2Cl_2(s) + 2e^- \Rightarrow 2Hg + 2Cl^-$		0.2676
$AgCl(s) + e^- \Rightarrow Ag + Cl^-$		0.2223
$SbO^+ + 2H^+ + 3e^- \Rightarrow Sb + H_2O$		0.212
$CuCl_3^{2-} + e^- \Rightarrow Cu + 3Cl^-$		0.178
$SO_4^{2-} + 4H^+ + 2e^- \Rightarrow SO_2(aq) + 2H_2O$		0.17
$Sn^{4+} + 2e^- \Rightarrow Sn^{2+}$		0.154
$S + 2H^+ + 2e^- \Rightarrow H_2S(g)$		0.141
$TiO^{2+} + 2H^+ + e^- \Rightarrow Ti^{3+} + H_2O$		0.10
$S_4O_6^{2-} + 2e^- \Rightarrow 2S_2O_3^{2-}$		0.08
$AgBr(s) + e^- \Rightarrow Ag + Br^-$		0.071
$2H^+ + 2e^- \Rightarrow H_2$		0.00
$Pb^{2+} + 2e^- \Rightarrow Pb$		-0.126
$Sn^{2+} + 2e^- \Rightarrow Sn$		-0.136
$AgI(s) + e^- \Rightarrow Ag + I^-$		-0.152
$Mo^{3+} + 3e^- \Rightarrow Mo$		-0.2
$N_2 + 5H^+ + 4e^- \Rightarrow H_2NNH_3^+$		-0.23
$Ni^{2+} + 2e^- \Rightarrow Ni$		-0.246
$V^{3+} + e^- \Rightarrow V^{2+}$		-0.255

**Standard Reduction Electrode Potentials for Inorganic  
Systems in Aqueous Solutions at 25°C (continued)**

Half Reaction		E°, V
$\text{Co}^{2+} + 2\text{e}^-$	$\Rightarrow \text{Co}$	-0.277
$\text{Ag}(\text{CN})_2^- + \text{e}^-$	$\Rightarrow \text{Ag} + 2\text{CN}^-$	-0.31
$\text{Cd}^{2+} + 2\text{e}^-$	$\Rightarrow \text{Cd}$	-0.403
$\text{Cr}^{3+} + \text{e}^-$	$\Rightarrow \text{Cr}^{2+}$	-0.41
$\text{Fe}^{2+} + 2\text{e}^-$	$\Rightarrow \text{Fe}$	-0.440
$2\text{CO}_2 + 2\text{H}^+ + 2\text{e}^-$	$\Rightarrow \text{H}_2\text{C}_2\text{O}_4$	-0.49
$\text{H}_3\text{PO}_3 + 2\text{H}^+ + 2\text{e}^-$	$\Rightarrow \text{H}_3\text{PO}_2 + \text{H}_2\text{O}$	-0.50
$\text{U}^{4+} + \text{e}^-$	$\Rightarrow \text{U}^{3+}$	-0.61
$\text{Zn}^{2+} + 2\text{e}^-$	$\Rightarrow \text{Zn}$	-0.763
$\text{Cr}^{2+} + 2\text{e}^-$	$\Rightarrow \text{Cr}$	-0.91
$\text{Mn}^{2+} + 2\text{e}^-$	$\Rightarrow \text{Mn}$	-1.18
$\text{Zr}^{4+} + 4\text{e}^-$	$\Rightarrow \text{Zr}$	-1.53
$\text{Ti}^{3+} + 3\text{e}^-$	$\Rightarrow \text{Ti}$	-1.63
$\text{Al}^{3+} + 3\text{e}^-$	$\Rightarrow \text{Al}$	-1.66
$\text{Th}^{4+} + 4\text{e}^-$	$\Rightarrow \text{Th}$	-1.90
$\text{Mg}^{2+} + 2\text{e}^-$	$\Rightarrow \text{Mg}$	-2.37
$\text{La}^{3+} + 3\text{e}^-$	$\Rightarrow \text{La}$	-2.52
$\text{Na}^+ + \text{e}^-$	$\Rightarrow \text{Na}$	-2.714
$\text{Ca}^{2+} + 2\text{e}^-$	$\Rightarrow \text{Ca}$	-2.87
$\text{Sr}^{2+} + 2\text{e}^-$	$\Rightarrow \text{Sr}$	-2.89
$\text{K}^+ + \text{e}^-$	$\Rightarrow \text{K}$	-2.925
$\text{Li}^+ + \text{e}^-$	$\Rightarrow \text{Li}$	-3.045

## STANDARD REDUCTION ELECTRODE POTENTIALS FOR INORGANIC SYSTEMS IN NONAQUEOUS SOLUTIONS AT 25°C

The following table lists some standard electrode potentials (in V) in various solvents. The rubidium ion, which possesses a large radius and shows a low deformability, has a rather low and constant solvation energy in all solvents.<sup>1</sup> As a result, the rubidium electrode is taken as a standard reference electrode in all solvents.

### REFERENCES

1. Koryta, J., Dvorák, J., and Bohácková, V., *Electrochemistry*, Methuen and Co., London, 1970.

**Standard Reduction Electrode Potentials for Inorganic Systems  
in Nonaqueous Solutions at 25°C**

System	H <sub>2</sub> O	CH <sub>3</sub> OH	CH <sub>3</sub> CN	HCOOH	N <sub>2</sub> H <sub>4</sub>	NH <sub>3</sub>
Li/Li <sup>+</sup>	-0.03	-0.16	-0.06	-0.03	-0.19	-0.35
Rb/Rb <sup>+</sup>	0.00	0.00	0.00	0.00	0.00	0.00
Cs/Cs <sup>+</sup>	+0.06	—	+0.01	-0.01	—	-0.02
K/K <sup>+</sup>	+0.06	—	+0.01	+0.10	-0.01	-0.05
Ca/Ca <sup>+2</sup>	+0.14	—	+0.42	+0.25	+0.10	+0.29
Na/Na <sup>+</sup>	+0.27	+0.21	+0.30	+0.03	+0.18	+0.08
Zn/Zn <sup>+2</sup>	+2.22	+2.20	+2.43	+2.40	+1.60	+1.40
Cd/Cd <sup>+2</sup>	+2.58	+2.51	+2.70	+2.70	+1.91	+1.73
Tl/Tl <sup>+</sup>	+2.64	+2.56	—	—	—	—
Pb/Pb <sup>+2</sup>	+2.85	+2.74	+3.05	+2.73	+2.36	+2.25
H <sub>2</sub> /H <sup>+</sup>	+2.98	+2.94	+3.17	+3.45	+2.01	+1.93
Cu/Cu <sup>+2</sup>	+3.32	+3.28	+2.79	+3.31	—	+2.36
Cu/Cu <sup>+</sup>	+3.50	—	+2.89	—	+2.23	+2.34
Hg/Hg <sup>+2</sup>	+3.78	+3.68	—	+3.63	—	—
Ag/Ag <sup>+</sup>	+3.78	+3.70	+3.40	+3.62	+2.78	+2.76
Hg/Hg <sup>+2</sup>	+3.84	—	+3.42	—	—	+2.08
I <sup>-</sup> /I <sub>2</sub>	+3.52	+3.30	+3.24	+3.42	—	+3.38
Br <sup>-</sup> /Br <sub>2</sub>	+4.04	+3.83	+3.64	+3.97	—	+3.76
Cl <sup>-</sup> /Cl <sub>2</sub>	+4.34	+4.16	+3.75	+4.22	—	+3.96

## REDOX POTENTIALS FOR SOME BIOLOGICAL HALF REACTIONS

The following table lists the standard redox potentials of some common biological half reactions (in V) at 298 K and pH = 7.0.<sup>1</sup>

### REFERENCES

1. Hibbert, D.B. and James, A.M., *Dictionary of Electrochemistry*, 2nd ed., John Wiley & Sons, New York, 1984.

Redox Potentials for Some Biological Half Reactions		
Biological System	Half-Cell Reaction	E°, V
Acetate/pyruvate	$\text{CH}_3\text{COOH} + \text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CH}_3\text{COCOOH} + \text{H}_2\text{O}$	-0.70
$\text{Fe}^{+3}/\text{Fe}^{+2}$ (ferredoxin)	$\text{Fe}^{+3} + \text{e}^- \rightarrow \text{Fe}^{+2}$	-0.432
$\text{H}^+/\text{H}_2$	$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$	-0.421
$\text{NADP}^+/\text{NADPH}$	$\text{NADP}^+ + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{NADPH} + \text{H}^+$	-0.324
$\text{NAD}^+/\text{NADH}$	$\text{NAD}^+ + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{NADH} + \text{H}^+$	-0.320
$\text{FAD}/\text{FADH}_2$	$\text{FAD} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{FADH}_2$	-0.219
Acetaldehyde/ethanol	$\text{CH}_3\text{CHO} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CH}_3\text{CH}_2\text{OH}$	-0.197
Pyruvate/lactate	$\text{CH}_3\text{COCOOH} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CH}_3\text{CH}(\text{OH})\text{COOH}$	-0.185
Oxaloacetate/malate		-0.166
	$\begin{array}{c} \text{CH}_2\text{COOH} \\   \\ \text{O}=\text{C}-\text{COOH} \end{array} + 2\text{H}^+ + 2\text{e}^- \rightarrow \begin{array}{c} \text{CH}_2\text{COOH} \\   \\ \text{HOCHCOOH} \end{array}$	
Methylene Blue (ox) (MB)/ Methylene Blue (red) (MBH <sub>2</sub> )	$\text{MB} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{MBH}_2$	0.011
Fumarate/succinate		0.031
	$\begin{array}{c} \text{CHCOOH} \\    \\ \text{CHCOOH} \end{array} + 2\text{H}^+ + 2\text{e}^- \rightarrow \begin{array}{c} \text{CH}_2\text{COOH} \\   \\ \text{CH}_2\text{COOH} \end{array}$	
$\text{Fe}^{+3}/\text{Fe}^{+2}$ (myoglobin)	$\text{Fe}^{+3} + \text{e}^- \rightarrow \text{Fe}^{+2}$	0.046
$\text{Fe}^{+3}/\text{Fe}^{+2}$ (cytochrome b)	$\text{Fe}^{+3} + \text{e}^- \rightarrow \text{Fe}^{+2}$	0.050
Ubiquinone/ubihydroquinone	$\text{Ub} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{UbH}_2$	0.10
(cytochrome c) <sup>+3</sup> /(cytochrome c) <sup>+2</sup>	$\text{Fe}^{+3} + \text{e}^- \rightarrow \text{Fe}^{+2}$	0.254
(cytochrome a) <sup>+3</sup> /(cytochrome a) <sup>+2</sup>	$\text{Fe}^{+3} + \text{e}^- \rightarrow \text{Fe}^{+2}$	0.29
(cytochrome f) <sup>+3</sup> /(cytochrome f) <sup>+2</sup>	$\text{Fe}^{+3} + \text{e}^- \rightarrow \text{Fe}^{+2}$	0.365
$\text{Cu}^{+2}/\text{Cu}^+$ (hemocyanin)	$\text{Cu}^{+2} + \text{e}^- \rightarrow \text{Cu}^+$	0.540
$\text{O}_2/\text{H}_2\text{O}$	$\text{O}_2(\text{g}) + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$	0.816

## STANDARD emf VALUES FOR THE CELL $\text{H}_2/\text{HCl}/\text{AgCl}$ , Ag IN VARIOUS AQUEOUS SOLUTIONS OF ORGANIC SOLVENTS AT VARIOUS TEMPERATURES

The table below lists the standard emf values of the cell  $\text{H}_2/\text{HCl}/\text{AgCl}$ , Ag in water as well as in various aqueous solutions of three common organic solvents, all alcohols, at different temperatures.<sup>1,2</sup> The compositions are given as mass percent of the alcohol in water. All emf values are expressed in volts.

### REFERENCES

1. Koryta, J., Dvorák, J., and Bohácková, V., *Electrochemistry*, Methuen and Co., London, 1970.
2. Robinson, R.A. and Stokes, R.H., *Electrolytic Solutions*, Butterworths, London, 1959.

Standard emf values for the Cell  $\text{H}_2/\text{HCl}/\text{AgCl}$ , Ag in Various Aqueous Solutions<sup>a</sup> of Organic Solvents at Various Temperatures

°C	100% Water	10% Aq. Methanol	10% Aq. Ethanol	10% Aq. 2-Propanol	20% Aq. Methanol	20% Aq. Ethanol	20% Aq. 2-Propanol
0	0.23655	0.22762	0.22726	0.22543	0.22022	0.21606	0.21612
5	0.23413	0.22547	0.22527	0.22365	0.21837	0.21486	0.21492
10	0.23142	0.22328	0.22328	0.22158	0.21631	0.21367	0.21336
15	0.22857	0.22085	0.22164	0.21922	0.21405	0.21190	0.21138
20	0.22557	0.21821	0.21901	0.21667	0.21155	0.21013	0.20906
25	0.22234	0.21535	0.21467	0.21383	0.20881	0.20757	0.20637
30	0.21904	0.21220	0.21383	0.21081	0.20567	0.20587	0.20341
35	0.21565	0.20892	0.21082	0.20754	0.20246	0.20275	0.20009
40	0.21208	0.20350	0.20783	0.20410	0.19910	0.19962	0.19652

<sup>a</sup> The percentages provided above are expressed as (vol/vol).

## TEMPERATURE DEPENDENCE OF THE STANDARD POTENTIAL OF THE SILVER CHLORIDE ELECTRODE

The following table gives the standard potential (in V) of the silver chloride electrode (saturated KCl) at different temperatures (in °C).<sup>1,2</sup> The uncertainty is  $\pm 0.05$  mV.

### REFERENCES

1. Conway, B.E., *Theory and Principles of Electrode Process*, Ronald Press, New York, 1965.
2. Koryta, J., Dvorák, J., and Bohácková, V., *Electrochemistry*, Methuen and Co., London, 1970.

**Temperature Dependence of the Standard Potential of the Silver Chloride Electrode**

Temperature (°C)	E°,V	Temperature (°C)	E°,V
0	0.23634	35	0.21563
5	0.23392	40	0.21200
10	0.23126	45	0.20821
15	0.22847	50	0.20437
20	0.22551	55	0.20035
25	0.22239	60	0.19620
30	0.21912		

## STANDARD ELECTRODE POTENTIALS OF ELECTRODES OF THE FIRST KIND

The following table lists the standard electrode potentials (in V) of some electrodes of the first kind.<sup>1-3</sup> These are divided into cationic and anionic electrodes. In cationic electrodes, equilibrium is established between atoms or molecules of the substance and the corresponding cations in solution. Examples include metal, amalgam, and the hydrogen electrode. In anionic electrodes, equilibrium is achieved between molecules and the corresponding anions in solution. The potential of the electrode is given by the Nernst equation in the form

$$E = E^0 + (RT)/(Z_{\pm}F) \ln a_{\pm}$$

where:

$E^0$  = standard electrode potential (in V)

R = gas constant

T = temperature (in K)

$Z_{\pm}$  = charge, with sign, of the cation (+) or anion (–)

F = Faraday

$a_{\pm}$  = activity of the cation (+) or anion (–)

Note that the equation uses the natural logarithm of the activity.

Electrodes of the first kind differ distinctly from the redox electrodes in that in the latter case, both oxidation states can be present in variable concentrations, while in electrodes of the first kind, one of the oxidation states is the electrode material.

## REFERENCES

1. Koryta, J., Dvůrák, J., and Karan, L., *Principles of Electrochemistry*, 2nd ed., John Wiley & Sons, New York, 1993.
2. Koryta, J., Dvůrák, J., and Bohácková, V., *Electrochemistry*, Methuen and Co., London, 1970.
3. Lide, D.R., Ed., *CRC Handbook of Chemistry and Physics*, 83rd ed., CRC Press, Boca Raton, FL, 2002.

Standard Electrode Potentials of Electrodes of the First Kind

Electrode	$E^0(\text{V})^a$	Electrode	$E^0(\text{V})^a$
Li <sup>+</sup> /Li	–3.0403	Ni <sup>2+</sup> /Ni	–0.23
Rb <sup>+</sup> /Rb	–2.98	In <sup>+</sup> /In	–0.203
Cs <sup>+</sup> /Cs	–2.92	Sn <sup>2+</sup> /Sn	–0.1377
K <sup>+</sup> /K	–2.931	Pb <sup>2+</sup> /Pb	–0.1264
Ba <sup>2+</sup> /Ba	–2.912	Cu <sup>2+</sup> /Cu	+0.3417
Sr <sup>2+</sup> /Sr	–2.89	Cu <sup>+</sup> /Cu	+0.52
Ca <sup>2+</sup> /Ca	–2.868	Te <sup>4+</sup> /Te	+0.56
Na <sup>+</sup> /Na	–2.71	Hg <sup>2+</sup> /Hg	+0.851
Mg <sup>2+</sup> /Mg	–2.372	Ag <sup>+</sup> /Ag	+0.7994
Be <sup>2+</sup> /Be	–1.847	Au <sup>3+</sup> /Au	+1.42
Al <sup>3+</sup> /Al	–1.662	Pt, Se <sup>–2</sup> /Se	–0.78
Zn <sup>2+</sup> /Zn	–0.7620	Pt, S <sup>–2</sup> /S	–0.51
Fe <sup>2+</sup> /Fe	–0.447	Pt, OH <sup>–</sup> /O <sub>2</sub> (g)	+0.401
Cd <sup>2+</sup> /Cd	–0.4032	Pt, I <sup>–</sup> /I <sub>2</sub>	+0.536
In <sup>3+</sup> /In	–0.3384	Pt, Br <sup>–</sup> /Br <sub>2</sub>	+1.066
Tl <sup>+</sup> /Tl	–0.336	Pt, Cl <sup>–</sup> /Cl <sub>2</sub> (g)	+1.35793
Co <sup>2+</sup> /Co	–0.27	Pt, F <sup>–</sup> /F <sub>2</sub> (g)	+2.866

## STANDARD ELECTRODE POTENTIALS OF ELECTRODES OF THE SECOND KIND

The following table lists the standard electrode potentials (in V) of some electrodes of the second kind.<sup>1-3</sup> These consist of three phases. The metal is covered by a layer of its sparingly soluble salt and is immersed in a solution of a soluble salt of the anion. Equilibrium is established between the metal atoms and the solution anions through two partial equilibria: one between the metal and its cation in the sparingly soluble salt and the other between the anion in the solid phase of the sparingly soluble salt and the anion in solution. The silver chloride electrode is preferred for precise measurements.

### REFERENCES

1. Koryta, J., Dvorák, J., and Karan, L., *Principles of Electrochemistry*, 2nd ed., John Wiley & Sons, New York, 1993.
2. Koryta, J., Dvorák, J., and Bohácková, V., *Electrochemistry*, Methuen and Co., London, 1970.
3. Lide, D.R., Ed., *CRC Handbook of Chemistry and Physics*, 83rd ed., CRC Press, Boca Raton, FL, 2002.

**Standard Electrode Potentials of Electrodes of the Second Kind**

Electrode	E°(V) <sup>a</sup>
PbSO <sub>4</sub> , SO <sub>4</sub> <sup>-2</sup> /Pb, Hg	-0.351
AgI, I <sup>-</sup> /Ag	-0.152
AgBr, Br <sup>-</sup> /Ag	+0.071
HgO, OH <sup>-</sup> /Hg	+0.0975
Hg <sub>2</sub> Br <sub>2</sub> , Br <sup>-</sup> /Hg	+0.140
AgCl, Cl <sup>-</sup> /Ag	+0.22216
Hg <sub>2</sub> Cl <sub>2</sub> , Cl <sup>-</sup> /Hg	+0.26791
Hg <sub>2</sub> SO <sub>4</sub> , SO <sub>4</sub> <sup>-2</sup> /Hg	+0.6123
PbO <sub>2</sub> , PbSO <sub>4</sub> , SO <sub>4</sub> <sup>-2</sup> /Pb	+1.6912



## POLAROGRAPHIC HALF-WAVE POTENTIALS ( $E_{1/2}$ ) OF INORGANIC CATIONS

The following table lists the polarographic half-wave potentials ( $E_{1/2}$ , in volts, vs. SCE, the standard calomel electrode) of inorganic cations and the supporting electrolyte used during the determination.<sup>1-6</sup> All supporting electrolyte solutions are aqueous unless noted. See page 629 for a description of the concentration nomenclature.

### REFERENCES

1. Skoog, D.A., West, D.M., and Holler, F.J., *Analytical Chemistry: An Introduction*, 6th ed., Saunders, Philadelphia, 1994.
2. Vogel, A.I., *A Textbook for Quantitative Inorganic Analysis*, 3rd ed., John Wiley & Sons, New York, 1968.
3. Fritz, J.S. and Schenk, G.H., *Quantitative Analytical Chemistry*, 4th ed., Prentice Hall, Englewood Cliffs, 1987.
4. Christian, G.D., *Analytical Chemistry*, 5th ed., John Wiley & Sons, New York, 1994.
5. Ewing, G.W., *Instrumental Methods of Analysis*, 5th ed., McGraw-Hill, New York, 1985.
6. Meites, L., *Polarographic Techniques*, 2nd ed., Wiley Interscience, New York, 1965.

# Supporting Electrolytes

Cation	KCl (0.1 F)	NH <sub>3</sub> (1 F) NH <sub>4</sub> Cl (1 F)	NaOH (1 F)	H <sub>3</sub> PO <sub>4</sub> (7.3 F)	KCN (1 F)	(CH <sub>3</sub> ) <sub>4</sub> NCl (0.1 F)	HCl (1 F)	H <sub>2</sub> SO <sub>4</sub> (0.5 M)	0.5 M Tartrate and		Others
									NaOH (0.1 F)	pH = 4.5	
Ba <sup>+2</sup>						-1.94					
Bj <sup>+3</sup>							-0.09	-0.04	-1.00	-0.23	
Cd <sup>+2</sup>	-0.64 (-0.60)	-0.81	-0.78	-0.77	-1.18						HNO <sub>3</sub> (1.0 F), -0.59 KI (1.0 F), -0.74 Pyridine (0.1 F)/ pyridinium (0.1 F), -1.07
Co <sup>+2</sup>	-1.20	-1.29	-1.46	-1.20	-1.45						
Cr <sup>+3</sup>		-1.43 (to Cr <sup>+2</sup> ) -1.71 (to Cr <sup>0</sup> )		-1.02 (to Cr <sup>+2</sup> )	-1.38 (to Cr <sup>+2</sup> )						
Cu <sup>+2</sup>	+0.04 (to Cu <sup>+</sup> ) -0.22 (to Cu <sup>0</sup> )	-0.24 (to Cu <sup>+</sup> ) -0.51 (to Cu <sup>0</sup> )	-0.41	-0.09	No reaction					-0.09	
Fe <sup>+2</sup>	-1.3	-1.49									
Fe <sup>+3</sup>			-1.12 (to Fe <sup>+2</sup> ) -1.74 (to Fe <sup>0</sup> )	+0.06 (to Fe <sup>+2</sup> )					-1.20, -1.73		EDTA (0.1 F)/ CH <sub>3</sub> COONa (2.0 F), -0.17, -1.30
K <sup>+</sup>											(CH <sub>3</sub> ) <sub>4</sub> NOH (0.1 M, 50% C <sub>2</sub> H <sub>5</sub> OH), -2.10
Li <sup>+</sup>											(CH <sub>3</sub> ) <sub>4</sub> NOH (0.1 M, 50% C <sub>2</sub> H <sub>5</sub> OH), -2.31 H <sub>2</sub> P <sub>2</sub> O <sub>7</sub> <sup>-2</sup> (0.2 M), pH = 2.2, +0.1
Mn <sup>+2</sup>	-1.51										

## Supporting Electrolytes (continued)

Cation	KCl (0.1 F)	NH <sub>3</sub> (1 F) NH <sub>4</sub> Cl (1 F)	NaOH (1 F)	H <sub>3</sub> PO <sub>4</sub> (7.3 F)	KCN (1 F)	(CH <sub>3</sub> ) <sub>4</sub> NCl (0.1 F)	HCl (1 F)	H <sub>2</sub> SO <sub>4</sub> (0.5 M)	0.5 M Tartrate and		Others
									NaOH (0.1 F)	pH = 4.5	
Na <sup>+</sup>						−2.07					
Ni <sup>+2</sup>	−1.1	−1.10			−1.36						KSCN (1.0 F), −0.7; pyridine (1.0 F)/HCl, pH = 7, −0.78
O <sub>2</sub>											pH = 1–10 (buffered), −0.05 and −0.90
Pb <sup>+2</sup>	−0.40		−0.75		−0.72				−0.75	−0.48	HNO <sub>3</sub> (1 F), −0.40
Sn <sup>+2</sup>							−0.47				F <sup>−</sup> (0.1 F), −0.611; F <sup>−</sup> (0.5 F), −0.683
Sn <sup>+4</sup>			−0.75								HCl (1.0 F)/NH <sub>4</sub> <sup>+</sup> (4.0 F), −0.25 and −0.52
Te <sup>+</sup>	−0.48	−0.48	−0.48								
Zn <sup>+2</sup>	−1.00	−1.34	−1.53						−1.15		

## POLAROGRAPHIC $E_{1/2}$ RANGES (IN V vs. SCE) FOR THE REDUCTION OF BENZENE DERIVATIVES

The following table lists the polarographic  $E_{1/2}$  potential ranges (in V vs. SCE) obtained at pH = 5–9 in unbuffered media in the reduction of benzene derivatives.<sup>1</sup>

### REFERENCES

1. Zuman, P., *The Elucidation of Organic Electrode Processes*, Academic Press, New York, 1969.

**Polarographic  $E_{1/2}$  Ranges (in V vs. SCE) for the Reduction of Benzene Derivatives**

Benzene Derivative <sup>a</sup>	Formula <sup>a</sup>	Polarographic $E_{1/2}$ Potential Range <sup>b</sup>
Diaryl alkene	ArCH=CHAr	–1.8 to –2.3
Methyl aryl ester	ArCOOCH <sub>3</sub>	–1.0 to –2.4
Aryl iodide	ArI	–1.2 to –1.9
Aryl methyl ketone	ArCOCH <sub>3</sub>	–1.1 to –1.8
Aromatic aldehyde	ArCHO	–1.1 to –1.7
Methyl $\alpha,\beta$ -unsaturated aryl ketone	ArCH=CHCOCH <sub>3</sub>	–1.0 to –1.6
Diaryl ketone	ArCOAr	–0.7 to –1.4
Azobenzenes	ArN=NAr	–0.3 to –0.8
Nitroarenes	ArNO <sub>2</sub>	–0.3 to –0.7
Nitrosoarenes	ArNO	–0.1 to –0.4
Diaryl iodonium salts	Ar <sub>2</sub> I <sup>+</sup>	–0.2 to –0.3

<sup>a</sup> Ar = aromatic ring.

<sup>b</sup> In V vs. SCE.

## VAPOR PRESSURE OF MERCURY

The following table provides data on the vapor pressure of mercury, useful for assessing and controlling the hazards associated with use of mercury as an electrode.<sup>1</sup>

### REFERENCES

1. Lide, D.R., Ed., *CRC Handbook of Chemistry and Physics*, 83rd ed., CRC Press, Boca Raton, FL, 2002.

Vapor Pressure of Mercury					
Temperature, °C	Vapor Pressure, mmHg	Vapor Pressure, Pa	Temperature, °C	Vapor Pressure, mmHg	Vapor Pressure, Pa
0	0.000185	0.0247	28	0.002359	0.3145
10	0.000490	0.0653	30	0.002777	0.3702
20	0.001201	0.1601	40	0.006079	0.8105
22	0.001426	0.1901	50	0.01267	1.689
24	0.001691	0.2254	100	0.273	36.4
26	0.002000	0.2666			

## ORGANIC FUNCTIONAL GROUP ANALYSIS OF NONPOLAROGRAPHIC ACTIVE GROUPS

Often an organic functional group is not (or may not be) reduced polarographically at an accessible potential range. In this case it is necessary to convert this functional group to a derivative whose reduction is feasible within such an accessible potential range. The table below lists the most common functional groups, the reagent needed, and the polarographically active derivative as well as the polarographically active group.<sup>1-4</sup> Such conversions enlarge the number of organic compounds that can be determined by polarography.

### REFERENCES

1. Svoronos, P., Horak, V., and Zuman, P., Polarographic study of structure-properties relationship of p-tosyl sulfilimines, phosphorus, *Sulfur Silicon*, 42, 139, 1989.
2. Willard, H.H., Dean, J.A., Settle, F.A., and Merritt, L.L., *Instrumental Methods of Analysis*, 7th ed., Wadsworth Publishing Co., Belmont, CA, 1995.
3. Zuman, P., *Chemical and Engineering News*, March 18, 1968, p. 94.
4. Zuman, P., *Substituent Effects in Organic Polarography*, Plenum, New York, 1967.

### Organic Functional Group Analysis of Nonpolarographic Active Groups

Functional Group	Reagent	Polarographically Active Derivative	Active Polarographic Group
Carbonyl (aldehyde, ketone), $>\text{C}=\text{O}$	Semicarbazide $\text{H}_2\text{NHC(=O)NH}_2$	$>\text{C}=\text{N}-\text{NHC(=O)NH}_2$	Semicarbazide, $>\text{C}=\text{N}-\text{N}$
	Hydroxylamine $\text{H}_2\text{NOH}$	$>\text{C}=\text{N}-\text{OH}$	Oxime, $>\text{C}=\text{N}-\text{OH}$
Primary amine, $\text{R}-\text{NH}_2$	Piperonal $\text{C}_8\text{H}_6\text{O}_3$	$\text{C}_7\text{H}_3\text{O}_2-\text{CH}=\text{N}-\text{R}$	Azomethine, $>\text{C}=\text{N}-\text{R}$
	Carbon disulfide, $\text{CS}_2$	$\text{R}-\text{N}=\text{C}(\text{S}-\text{H})_2$	Dithiocarbonate $-\text{N}=\text{C}(\text{S}^-)_2$
	Cupric phosphate, $\text{Cu}_3(\text{PO}_4)_2$ , suspension	$[\text{Cu}^{+2}-\text{amine}]$ complex	$[\text{Cu}^{+2}-\text{amine complex}]$
Secondary amine, $\text{R}_2\text{NH}$	Nitrous acid, $\text{HNO}_2$	$\text{R}_2\text{N}-\text{N}=\text{O}$	Nitroso, $\text{N}-\text{N}=\text{O}$
Primary alcohols, $\text{R}-\text{CH}_2\text{OH}$	Chromic acid, $\text{HCrO}_4$	$\text{R}-\text{CHO}$	Aldehyde carbonyl, $\text{R}-\text{C}(=\text{O})\text{H}$
Secondary alcohols, $\text{R}_2-\text{CH}_2\text{OH}$	Chromic acid, $\text{HCrO}_4$	$\text{R}_2\text{C}=\text{O}$	Ketone carbonyl, $\text{R}-\text{C}(=\text{O})-\text{R}$
1,2-Diols	Periodic acid, $\text{HIO}_4$	$\text{R}-\text{C}(=\text{O})\text{H}$ and $\text{R}-\text{C}(=\text{O})-\text{R}$	Aldehyde and/or ketone carbonyl $>\text{C}=\text{O}$
Carboxylic acid, $\text{R}-\text{C}(=\text{O})\text{OH}$	Thiourea, $(\text{H}_2\text{N})_2\text{C}=\text{S}$	$\text{RCO}_2^-[(\text{H}_2\text{N})_2\text{CSH}]^+$	Protonated thiocarbonyl, $[>\text{C}=\text{S}-\text{H}]^+$
Phenyl, $\text{C}_6\text{H}_5-$ , $\phi$	Conc. nitric/conc. sulfuric acid, $\text{HNO}_3/\text{H}_2\text{SO}_4$	$\text{C}_6\text{H}_5\text{NO}_2$	Nitro, $-\text{NO}_2$
Sulfides (thioethers), $>\text{S}$	Hydrogen peroxide, $\text{H}_2\text{O}_2$ or <i>m</i> -chloroperbenzoic acid, $1,3\text{-Cl-C}_6\text{H}_4\text{-COOH}$	$>\text{S}^+ \rightarrow \text{O}^-$	Sulfoxide, $\text{S}^+ - \text{O}^-$
	Chloramine-T, $\text{CH}_3-\phi-\text{SO}_2\text{NCINa}$	$>\text{S}=\text{NSO}_2-\text{C}_6\text{H}_4-\text{CH}_3$	Sulfilimine, $>\text{S}=\text{N}-$

## COULOMETRIC TITRATIONS

The following table lists some common coulometric (also known as constant-current coulometry) titrations.<sup>1-4</sup> Since the titrant is generated electrolytically and reacted immediately, the method gets widespread applications. The generating electrolytic concentrations need to be only approximate, while unstable titrants are consumed as soon as they are formed. The technique is more accurate than methods where visual end points are required, such as in the case of indicators. The unstable titrants in the table below are marked with an asterisk.

## REFERENCES

1. Christian, G.D., *Analytical Chemistry*, 5th ed., John Wiley & Sons, New York, 1994.
2. Christian, G.D., Electrochemical methods for analysis of enzyme systems, in *Advances in Biomedical Engineering and Medical Physics*, Vol. 4, Levine, S.N., Ed., Wiley Interscience, New York, 1971, p. 95.
3. Skoog, D.A., West, D.M., and Holler, J.F., *Fundamentals of Analytical Chemistry*, 6th ed., Saunders, Philadelphia, 1996.
4. Harris, D.C., *Quantitative Chemical Analysis*, 5th ed., W.H. Freeman, San Francisco, 1998.

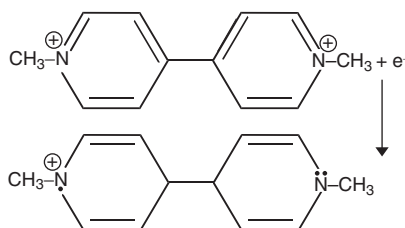


### Coulometric Titrations

Reagent	Generator Electrode Reaction	Typical Generating Electrolyte	Substances Determined
Ag <sup>+</sup>	$\text{Ag} \rightarrow \text{Ag}^+ + \text{e}^-$	Ag anode in HNO <sub>3</sub>	Br <sup>-</sup> , Cl <sup>-</sup> , thiols
Ag <sup>+2</sup>	$\text{Ag}^+ \rightarrow \text{Ag}^{+2} + \text{e}^-$		Ce <sup>+3</sup> , V <sup>+4</sup> , H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> , As <sup>+3</sup>
*Biphenyl radical anion	$(\text{C}_6\text{H}_5)_2 + \text{e}^- \rightarrow (\text{C}_6\text{H}_5)_2^-$	Biphenyl/(CH <sub>3</sub> ) <sub>4</sub> NBr in DMF	Anthracene
*Br <sub>2</sub>	$2 \text{Br}^- \rightarrow \text{Br}_2 + 2\text{e}^-$	0.2 M NaBr in 0.1 M H <sub>2</sub> SO <sub>4</sub>	As <sup>+3</sup> , Sb <sup>+3</sup> , U <sup>+4</sup> , Tl <sup>+</sup> , I <sup>-</sup> , SCN <sup>-</sup> , NH <sub>2</sub> OH, N <sub>2</sub> H <sub>4</sub> , phenols, aromatic amines, mustard gas, olefins, 8-hydroxy-quinoline
*BrO <sup>-</sup>	$\text{Br}^- + 2 \text{OH}^- \rightarrow \text{BrO}^- + \text{H}_2\text{O} + 2\text{e}^-$	1 M NaBr in borate buffer, pH = 8.6 <sup>a</sup>	NH <sub>3</sub>
Ce <sup>+4</sup>	$\text{Ce}^{+2} \rightarrow \text{Ce}^{+4} + 2\text{e}^-$	0.1 M CeSO <sub>4</sub> in 3 M H <sub>2</sub> SO <sub>4</sub>	Fe <sup>+2</sup> , Ti <sup>+3</sup> , U <sup>+4</sup> , As <sup>+3</sup> , I <sup>-</sup> , Fe(SCN) <sub>6</sub> <sup>-4</sup>
*Cl <sub>2</sub>	$2 \text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$		As <sup>+3</sup> , I <sup>-</sup>
*Cr <sup>+2</sup>	$\text{Cr}^{+3} + \text{e}^- \rightarrow \text{Cr}^{+2}$	Cr <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> in H <sub>2</sub> SO <sub>4</sub>	O <sub>2</sub>
*CuCl <sub>3</sub> <sup>-2</sup>	$\text{Cu}^{+2} + 3\text{Cl}^- + \text{e}^- \rightarrow \text{CuCl}_3^{-2}$	0.1 M CuSO <sub>4</sub> in 1 M HCl	V <sup>+5</sup> , Cr <sup>+6</sup> , IO <sub>3</sub> <sup>-</sup>
EDTA	$\text{HgNH}_3(\text{EDTA})^{+2} + \text{NH}_4^+ + 2\text{e}^- \rightarrow \text{Hg} + 2\text{NH}_3 + (\text{HEDTA})^{-3}$	0.02 M Hg <sup>+2</sup> /EDTA in ammoniacal buffer, pH = 8.5, Hg cathode	Ca <sup>+2</sup> , Cu <sup>+3</sup> , Zn <sup>+2</sup> , Pb <sup>+2</sup>
EGTA	$\text{HgNH}_3(\text{EGTA})^{+2} + \text{NH}_4^+ + 2\text{e}^- \rightarrow \text{Hg} + 2\text{NH}_3 + (\text{HEGTA})^{+1}$	0.1 M Hg <sup>+2</sup> /EGTA in triethanolamine, pH = 8.6, Hg cathode	Ca <sup>+2</sup> (in the presence of Mg <sup>+2</sup> )
Fe <sup>+2</sup>	$\text{Fe}^{+3} + \text{e}^- \rightarrow \text{Fe}^{+2}$	Acid solution of FeNH <sub>4</sub> (SO <sub>4</sub> ) <sub>2</sub>	Cr <sup>+6</sup> , Mn <sup>+7</sup> , V <sup>+5</sup> , Ce <sup>+4</sup>
I <sub>2</sub>	$2\text{I}^- \rightarrow \text{I}_2 + 2\text{e}^-$	0.2 M KI in pH = 8 buffer, pyridine, SO <sub>2</sub> , CH <sub>3</sub> OH, KI (Karl Fisher titration)	As <sup>+3</sup> , Sb <sup>+3</sup> , S <sub>2</sub> O <sub>3</sub> <sup>-2</sup> , H <sub>2</sub> S, H <sub>2</sub> O
H <sup>+</sup>	$2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + \text{O}_2 + 4\text{e}^-$	0.1 M Na <sub>2</sub> SO <sub>4</sub> (water electrolysis)	Pyridine
*Mn <sup>+3</sup>	$\text{Mn}^{+2} \rightarrow \text{Mn}^{+3} + \text{e}^-$	MnSO <sub>4</sub> in 2 M H <sub>2</sub> SO <sub>4</sub>	H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> , Fe <sup>+2</sup> , As <sup>+3</sup> , H <sub>2</sub> O <sub>2</sub>
Mo <sup>+5</sup>	$\text{Mo}^{+6} + \text{e}^- \rightarrow \text{Mo}^{+5}$	0.7 M Mo <sup>+6</sup> in 4 M H <sub>2</sub> SO <sub>4</sub>	Cr <sub>2</sub> O <sub>7</sub> <sup>-2</sup>
*MV <sup>+b</sup>	$\text{MV}^{+2} + \text{e}^- \rightarrow \text{MV}^+$		Mn <sup>+3</sup> (in enzymes)
OH <sup>-</sup>	$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$	0.1 M Na <sub>2</sub> SO <sub>4</sub> (water electrolysis)	HCl
Ti <sup>+3</sup>	Ti <sup>+4</sup> + e <sup>-</sup> → Ti <sup>+3</sup> or TiO <sup>+2</sup> + 2H <sup>+</sup> + e <sup>-</sup> → Ti <sup>+3</sup> + H <sub>2</sub> O	3.6 M TiCl <sub>4</sub> in 7 M HCl	V <sup>+5</sup> , Fe <sup>+3</sup> , Ce <sup>+4</sup> , U <sup>+6</sup>
U <sup>+4</sup>	$\text{UO}_2^{+2} + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{U}^{+4} + 2\text{H}_2\text{O}$	Acid solution of UO <sub>2</sub> <sup>+2</sup>	Cr <sup>+6</sup> , Ce <sup>+4</sup>

<sup>a</sup> See page 573 for the preparation of this buffer.

<sup>b</sup> MV<sup>+</sup> = methyl viologen radical cation; MV<sup>+2</sup> = methyl viologen radical cation.



## CHAPTER 7

# Ultraviolet Spectrophotometry

### CONTENTS

Solvents for Ultraviolet Spectrophotometry  
Ultraviolet Spectra of Common Liquids  
Transmittance–Absorbance Conversion  
Correlation Table of Ultraviolet Active Functionalities  
Woodward’s Rules for Bathochromic Shifts

## SOLVENTS FOR ULTRAVIOLET SPECTROPHOTOMETRY

The following table lists some useful solvents for ultraviolet spectrophotometry, along with their wavelength cutoffs and dielectric constants.<sup>1-6</sup>

### REFERENCES

1. Willard, H.H., Merritt, L.L., Dean, J.A., and Settle, F.A., *Instrumental Methods of Analysis*, 7th ed., Van Nostrand, New York, 1988.
2. Strobel, H.A. and Heinemann, W.R., *Chemical Instrumentation: A Systematic Approach*, 3rd ed., John Wiley & Sons, New York, 1989.
3. Dreisbach, R.R., *Physical Properties of Chemical Compounds*, Advances in Chemistry Series 15, American Chemical Society, Washington, D.C., 1955.
4. Dreisbach, R.R., *Physical Properties of Chemical Compounds*, Advances in Chemistry Series 22, American Chemical Society, Washington, D.C., 1959.
5. Sommer, L., *Analytical Absorption Spectrophotometry in the Visible and Ultraviolet*, Elsevier Science, Amsterdam, 1989.
6. Krieger, P.A., *High Purity Solvent Guide*, Burdick and Jackson, McGraw Park, IL, 1984.

### Solvents For Ultraviolet Spectrophotometry

Solvent	Wavelength Cutoff, nm	Dielectric Constant (20°C)
Acetic acid	260	6.15
Acetone	330	20.7 (25°C)
Acetonitrile	190	37.5
Benzene	280	2.284
<i>sec</i> -Butyl alcohol (2-butanol)	260	15.8 (25°C)
<i>n</i> -Butyl acetate	254	
<i>n</i> -Butyl chloride	220	7.39 (25°C)
Carbon disulfide	380	2.641
Carbon tetrachloride	265	2.238
Chloroform <sup>a</sup>	245	4.806
Cyclohexane	210	2.023
1,2-Dichloroethane	226	10.19 (25°C)
1,2-Dimethoxyethane	240	
<i>N,N</i> -Dimethylacetamide	268	59 (83°C)
<i>N,N</i> -Dimethylformamide	270	36.7
Dimethylsulfoxide	265	4.7
1,4-Dioxane	215	2.209 (25°C)
Diethyl ether	218	4.335
Ethanol	210	24.30 (25°C)
2-Ethoxyethanol	210	
Ethyl acetate	225	6.02 (25°C)
Methyl ethyl ketone	330	18.5
Glycerol	207	42.5 (25°C)
<i>n</i> -Hexadecane	200	2.06 (25°C)
<i>n</i> -Hexane	210	1.890
Methanol	210	32.63 (25°C)
2-Methoxyethanol	210	16.9
Methyl cyclohexane	210	2.02 (25°C)
Methyl isobutyl ketone	335	
2-Methyl-1-propanol	230	
<i>N</i> -Methyl-2-pyrrolidone	285	32.0
Pentane	210	1.844
<i>n</i> -Pentyl acetate	212	
<i>n</i> -Propyl alcohol	210	20.1 (25°C)
<i>sec</i> -Propyl alcohol	210	18.3 (25°C)
Pyridine	330	12.3 (25°C)
Tetrachloroethylene <sup>b</sup>	290	
Tetrahydrofuran	220	7.6
Toluene	286	2.379 (25°C)
1,1,2-Trichloro-1,2,2-trifluoroethane	231	
2,2,4-Trimethylpentane	215	1.936 (25°C)
<i>o</i> -Xylene	290	2.568
<i>m</i> -Xylene	290	2.374
<i>p</i> -Xylene	290	2.270
Water		78.54 (25°C)

<sup>a</sup> Stabilized with ethanol to avoid phosgene formation.

<sup>b</sup> Stabilized with thymol (isopropyl *meta*-cresol).

## ULTRAVIOLET SPECTRA OF COMMON LIQUIDS

The following table presents, in tabular form, the ultraviolet spectra of some common solvents and liquids used in chemical analysis. The data were obtained using a 1.00 cm path length cell, against a water reference.<sup>1,2</sup>

### REFERENCES

1. Krieger, P.A., *High Purity Solvent Guide*, Burdick and Jackson, McGraw Park, IL, 1984.
2. Sommer, L., *Analytical Absorption Spectrophotometry in the Visible and Ultraviolet*, Elsevier Science, Amsterdam, 1989

Ultraviolet Spectra of Common Liquids

Acetone		Benzene	
Wavelength, nm	Maximum Absorbance	Wavelength, nm	Maximum Absorbance
330	1.000	278	1.000
340	0.060	300	0.020
350	0.010	325	0.010
375	0.005	350	0.005
400	0.005	400	0.005
Acetonitrile		1-Butanol	
Wavelength, nm	Maximum Absorbance	Wavelength, nm	Maximum Absorbance
190	1.000	215	1.000
200	0.050	225	0.500
225	0.010	250	0.040
250	0.005	275	0.010
350	0.005	300	0.005
2-Butanol		Carbon Tetrachloride	
Wavelength, nm	Maximum Absorbance	Wavelength, nm	Maximum Absorbance
260	1.000	263	1.000
275	0.300	275	0.100
300	0.010	300	0.005
350	0.005	350	0.005
400	0.005	400	0.005
n-Butyl Acetate		Chlorobenzene	
Wavelength, nm	Maximum Absorbance	Wavelength, nm	Maximum Absorbance
254	1.000	287	1.000
275	0.050	300	0.050
300	0.010	325	0.040
350	0.005	350	0.020
400	0.005	400	0.005

**Ultraviolet Spectra of Common Liquids (continued)**

<b><i>n</i>-Butyl Chloride</b>		<b>Chloroform</b>	
<b>Wavelength, nm</b>	<b>Maximum Absorbance</b>	<b>Wavelength, nm</b>	<b>Maximum Absorbance</b>
220	1.000	245	1.000
225	0.300	250	0.300
250	0.010	275	0.005
300	0.005	300	0.005
400	0.005	400	0.005

<b>Cyclohexane</b>		<b><i>o</i>-Dichlorobenzene</b>	
<b>Wavelength, nm</b>	<b>Maximum Absorbance</b>	<b>Wavelength, nm</b>	<b>Maximum Absorbance</b>
200	1.000	295	1.000
225	0.170	300	0.300
250	0.020	325	0.100
300	0.005	350	0.050
400	0.005	400	0.005

<b>Cyclopentane</b>		<b>Diethyl Carbonate</b>	
<b>Wavelength, nm</b>	<b>Maximum Absorbance</b>	<b>Wavelength, nm</b>	<b>Maximum Absorbance</b>
200	1.000	256	1.000
215	0.300	265	0.150
225	0.020	275	0.050
300	0.005	300	0.040
400	0.005	400	0.010

<b>Decahydronaphthalene</b>		<b>Dimethyl Acetamide</b>	
<b>Wavelength, nm</b>	<b>Maximum Absorbance</b>	<b>Wavelength, nm</b>	<b>Maximum Absorbance</b>
200	1.000	268	1.000
225	0.500	275	0.300
250	0.050	300	0.080
300	0.005	350	0.005
400	0.005	400	0.005

<b>Dimethyl Formamide</b>		<b>2-Ethoxyethanol</b>	
<b>Wavelength, nm</b>	<b>Maximum Absorbance</b>	<b>Wavelength, nm</b>	<b>Maximum Absorbance</b>
268	1.000	210	1.000
275	0.300	225	0.500
300	0.050	250	0.200
350	0.005	300	0.005
400	0.005	400	0.005

<b>Dimethyl Sulfoxide</b>		<b>Ethyl Acetate</b>	
<b>Wavelength, nm</b>	<b>Maximum Absorbance</b>	<b>Wavelength, nm</b>	<b>Maximum Absorbance</b>
268	1.000	256	1.000
275	0.500	275	0.050
300	0.200	300	0.030
350	0.020	325	0.005
400	0.005	350	0.005

**Ultraviolet Spectra of Common Liquids (continued)**

<b>1,4-Dioxane</b>		<b>Diethyl Ether</b>	
<b>Wavelength, nm</b>	<b>Maximum Absorbance</b>	<b>Wavelength, nm</b>	<b>Maximum Absorbance</b>
215	1.000	215	1.000
250	0.300	250	0.080
300	0.020	275	0.010
350	0.005	300	0.005
400	0.005	400	0.005
<b>Ethylene Dichloride</b>		<b>Hexadecane</b>	
<b>Wavelength, nm</b>	<b>Maximum Absorbance</b>	<b>Wavelength, nm</b>	<b>Maximum Absorbance</b>
228	1.000	190	1.000
240	0.300	200	0.500
250	0.100	250	0.020
300	0.005	300	0.005
400	0.005	400	0.005
<b>Ethylene Glycol Dimethyl Ether (Glyme)</b>		<b>Hexane</b>	
<b>Wavelength, nm</b>	<b>Maximum Absorbance</b>	<b>Wavelength, nm</b>	<b>Maximum Absorbance</b>
220	1.000	195	1.000
250	0.250	225	0.050
300	0.050	250	0.010
350	0.010	275	0.005
400	0.005	300	0.005
<b>Heptane</b>		<b>Isobutanol</b>	
<b>Wavelength, nm</b>	<b>Maximum Absorbance</b>	<b>Wavelength, nm</b>	<b>Maximum Absorbance</b>
200	1.000	220	1.000
225	0.100	250	0.050
250	0.010	275	0.030
300	0.005	300	0.020
400	0.005	400	0.010
<b>Methanol</b>		<b>Methyl-<i>t</i>-Butyl Ether</b>	
<b>Wavelength, nm</b>	<b>Maximum Absorbance</b>	<b>Wavelength, nm</b>	<b>Maximum Absorbance</b>
205	1.000	210	1.000
225	0.160	225	0.500
250	0.020	250	0.100
300	0.005	300	0.005
400	0.005	400	0.005
<b>2-Methoxyethanol</b>		<b>Methylene Chloride</b>	
<b>Wavelength, nm</b>	<b>Maximum Absorbance</b>	<b>Wavelength, nm</b>	<b>Maximum Absorbance</b>
210	1.000	233	1.000
250	0.130	240	0.100
275	0.030	250	0.010
300	0.005	300	0.005
400	0.005	400	0.005

# Ultraviolet Spectra of Common Liquids (continued)

2-Methoxyethyl Acetate		Methyl Ethyl Ketone	
Wavelength, nm	Maximum Absorbance	Wavelength, nm	Maximum Absorbance
254	1.000	329	1.000
275	0.150	340	0.100
300	0.050	350	0.020
350	0.005	375	0.010
400	0.005	400	0.005
Methyl Isoamyl Ketone		<i>n</i> -Methylpyrrolidone	
Wavelength, nm	Maximum Absorbance	Wavelength, nm	Maximum Absorbance
330	1.000	285	1.000
340	0.100	300	0.500
350	0.050	325	0.100
375	0.010	350	0.030
400	0.005	400	0.010
Methyl Isobutyl Ketone		Pentane	
Wavelength, nm	Maximum Absorbance	Wavelength, nm	Maximum Absorbance
334	1.000	190	1.000
340	0.500	200	0.600
350	0.250	250	0.010
375	0.050	300	0.005
400	0.005	400	0.005
Methyl <i>n</i> -Propyl Ketone		$\beta$ -Phenethylamine	
Wavelength, nm	Maximum Absorbance	Wavelength, nm	Maximum Absorbance
331	1.000	285	1.000
340	0.150	300	0.300
350	0.020	325	0.100
375	0.005	350	0.050
400	0.005	400	0.005
1-Propanol		Pyridine	
Wavelength, nm	Maximum Absorbance	Wavelength, nm	Maximum Absorbance
210	1.000	330	1.000
225	0.500	340	0.100
250	0.050	350	0.010
300	0.005	375	0.010
400	0.005	400	0.005
2-Propanol		Tetrahydrofuran	
Wavelength, nm	Maximum Absorbance	Wavelength, nm	Maximum Absorbance
205	1.000	212	1.000
225	0.160	250	0.180
250	0.020	300	0.020
300	0.005	350	0.005
400	0.010	400	0.005



**Ultraviolet Spectra of Common Liquids (continued)**

<b>Propylene Carbonate</b>		<b>Toluene</b>	
<b>Wavelength, nm</b>	<b>Maximum Absorbance</b>	<b>Wavelength, nm</b>	<b>Maximum Absorbance</b>
280	1.000	284	1.000
300	0.500	300	0.120
350	0.050	325	0.020
375	0.030	350	0.050
400	0.020	400	0.005

<b>1,2,4-Trichlorobenzene</b>		<b>2,2,4-Trimethylpentane</b>	
<b>Wavelength, nm</b>	<b>Maximum Absorbance</b>	<b>Wavelength, nm</b>	<b>Maximum Absorbance</b>
308	1.000	215	1.000
310	0.500	225	0.100
350	0.050	250	0.020
375	0.010	300	0.005
400	0.005	400	0.005

<b>Trichloroethylene</b>		<b>Water</b>	
<b>Wavelength, nm</b>	<b>Maximum Absorbance</b>	<b>Wavelength, nm</b>	<b>Maximum Absorbance</b>
273	1.000	190	0.010
300	0.100	200	0.010
325	0.080	250	0.005
350	0.060	300	0.005
400	0.060	400	0.005

<b>1,1,2-Trichlorotrifluoroethane</b>		<b>o-Xylene</b>	
<b>Wavelength, nm</b>	<b>Maximum Absorbance</b>	<b>Wavelength, nm</b>	<b>Maximum Absorbance</b>
231	1.000	288	1.000
250	0.050	300	0.200
300	0.005	325	0.050
350	0.005	350	0.010
400	0.005	400	0.005

## TRANSMITTANCE–ABSORBANCE CONVERSION

The following is a conversion table for absorbance and transmittance, assuming no reflection. Included for each pair is the percent error propagated into a measured concentration (using the Beer–Lambert law), assuming an uncertainty in transmittance of +0.005.<sup>1</sup> The value of transmittance that will give the lowest percent error in concentration is 3.368. Where possible, analyses should be designed for the low uncertainty area.

## REFERENCES

1. Kennedy, J.H., *Analytical Chemistry Principles*, Harcourt, Brace and Jovanovich, San Diego, 1984.

Transmittance–Absorbance Conversion		
Transmittance	Absorbance	Percent Uncertainty
0.980	0.009	25.242
0.970	0.013	16.915
0.960	0.018	12.752
0.950	0.022	10.256
0.940	0.027	8.592
0.930	0.032	7.405
0.920	0.036	6.515
0.910	0.041	5.823
0.900	0.046	5.270
0.890	0.051	4.818
0.880	0.056	4.442
0.870	0.060	4.125
0.860	0.065	3.853
0.850	0.071	3.618
0.840	0.076	3.412
0.830	0.081	3.231
0.820	0.086	3.071
0.810	0.091	2.928
0.800	0.097	2.799
0.790	0.102	2.684
0.780	0.108	2.579
0.770	0.113	2.483
0.760	0.119	2.386
0.750	0.125	2.316
0.740	0.131	2.243
0.730	0.137	2.175
0.720	0.143	2.113
0.710	0.149	2.055
0.700	0.155	2.002
0.690	0.161	1.952
0.680	0.167	1.906
0.670	0.174	1.863
0.660	0.180	1.822
0.650	0.187	1.785
0.640	0.194	1.750
0.630	0.201	1.717
0.620	0.208	1.686
0.610	0.215	1.657
0.600	0.222	1.631
0.590	0.229	1.605
0.580	0.237	1.582

**Transmittance–Absorbance Conversion (continued)**

<b>Transmittance</b>	<b>Absorbance</b>	<b>Percent Uncertainty</b>
0.570	0.244	1.560
0.560	0.252	1.539
0.540	0.268	1.502
0.530	0.276	1.485
0.520	0.284	1.470
0.510	0.292	1.455
0.500	0.301	1.442
0.490	0.310	1.430
0.480	0.319	1.419
0.470	0.328	1.408
0.460	0.337	1.399
0.450	0.347	1.391
0.440	0.356	1.383
0.430	0.366	1.377
0.420	0.377	1.372
0.410	0.387	1.367
0.400	0.398	1.364
0.390	0.409	1.361
0.380	0.420	1.359
0.370	0.432	1.358
0.360	0.444	1.359
0.350	0.456	1.360
0.340	0.468	1.362
0.330	0.481	1.366
0.320	0.495	1.371
0.310	0.509	1.376
0.300	0.523	1.384
0.290	0.538	1.392
0.280	0.553	1.402
0.270	0.569	1.414
0.260	0.585	1.427
0.250	0.602	1.442
0.240	0.620	1.459
0.230	0.638	1.478
0.220	0.657	1.500
0.210	0.678	1.525
0.200	0.699	1.553
0.190	0.721	1.584
0.180	0.745	1.619
0.170	0.769	1.659
0.160	0.796	1.704
0.150	0.824	1.756
0.140	0.854	1.816
0.130	0.886	1.884
0.120	0.921	1.964
0.110	0.958	2.058
0.100	1.000	2.170
0.090	1.046	2.306
0.080	1.097	2.473
0.070	1.155	2.685
0.060	1.222	2.961
0.050	1.301	3.336
0.040	1.398	3.881
0.030	1.523	4.751
0.020	1.699	6.387
0.010	2.000	10.852

## CORRELATION TABLE FOR ULTRAVIOLET ACTIVE FUNCTIONALITIES

The following table presents a correlation between common chromophoric functional groups and the expected absorptions from ultraviolet spectrophotometry.<sup>1-3</sup> Although not as informative as infrared correlations, UV can often provide valuable qualitative information.


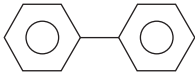

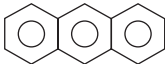

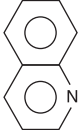
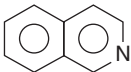
### REFERENCES

1. Willard, H.H., Dean, J.A., Settle, F.A., and Merritt, L.L., *Instrumental Methods of Analysis*, 7th ed., Wadsworth Publishing Co., Belmont, CA, 1995.
2. Silverstein, R.M. and Webster, F.X., *Spectrometric Identification of Organic Compounds*, 6th ed., Wiley, New York, 1998.
3. Lambert, J.B., Shurvell, H.F., Lightner, D.A., Verbit, L., and Cooks, R.G., *Organic Structural Spectroscopy*, Prentice Hall, Upper Saddle River, NJ, 1998.

Correlation Table for Ultraviolet Active Functionalities

Chromophore	Functional Group	$\gamma_{\max}$ , nm	$\epsilon_{\max}$	$\gamma_{\max}$ , nm	$\epsilon_{\max}$	$\gamma_{\max}$ , nm	$\epsilon_{\max}$
Ether	—O—	185	1000				
Thioether	—S—	194	4600	215	1600		
Amine	—NH <sub>2</sub> —	195	2800				
Amide	—CONH <sub>2</sub>	<210	—				
Thiol	—SH	195	1400				
Disulfide	—S—S—	194	5500	255	400		
Bromide	—Br	208	300				
Iodide	—I	260	400				
Nitrile	—C≡N	160	—				
Acetylide (alkyne)	—C≡C—	175–180	6000				
Sulfone	—SO <sub>2</sub> —	180	—				
Oxime	—NOH	190	5000				
Azido	>C=N—	190	5000				
Alkene	>C=C<	190	8000				
Ketone	>C=O	195	1000	270–285	18–30		
Thioketone	>C=S	205	Strong				
Esters	—COOR	205	50				
Aldehyde	—CHO	210	Strong	280–300	11–18		
Carboxyl	—COOH	200–210	50–70				
Sulfoxide	>S→O	210	1500				
Nitro	—NO <sub>2</sub>	210	Strong				
Nitrite	—ONO	220–230	1000–2000	300–4000	10		
Azo	—N=N—	285–400	3–25				
Nitroso	—N=O	302	100				
Nitrate	—ONO <sub>2</sub>	270 (shoulder)	12				
Conjugated hydrocarbon	—(C=C) <sub>2</sub> — (acyclic)	210–230	21,000				
Conjugated hydrocarbon	—(C=C) <sub>3</sub> —	260	35,000				
Conjugated hydrocarbon	—(C=C) <sub>4</sub> —	300	52,000				
Conjugated hydrocarbon	—(C=C) <sub>5</sub> —	330	118,000				
Conjugated hydrocarbon	—(C=C) <sub>2</sub> — (alicyclic)	230–260	3000–8000				
Conjugated hydrocarbon	C=C—C≡C	219	6500				
Conjugated system	C=C—C=N	220	23,000				

Correlation Table for Ultraviolet Active Functionalities (continued)

Chromophore	Functional Group	$\gamma_{\max}$ , nm	$\epsilon_{\max}$	$\gamma_{\max}$ , nm	$\epsilon_{\max}$	$\gamma_{\max}$ , nm	$\epsilon_{\max}$
Conjugated system	C=C-C=O	210–250	10,000–20,000			300–350	Weak
Conjugated system	C=C-NO <sub>2</sub>	229	9500				
Benzene		184	46,700	202	6900	255	170
Diphenyl				246	20,000		
Naphthalene		220	112,000	275	5600	312	175
Anthracene		252	199,000	375	7900		
Pyridine		174	80,000	195	6000	251	1700
Quinoline		227	37,000	270	3600	314	2750
Isoquinoline		218	80,000	266	4000	317	3500

## WOODWARD'S RULES FOR BATHOCHROMIC SHIFTS

Conjugated systems show bathochromic shifts in their  $\pi \rightarrow \pi^*$  transition bands. Empirical methods for predicting those shifts were originally formulated by Woodward, Fieser, and Fieser.<sup>1-4</sup> This section includes the most important conjugated system rules.<sup>1-5</sup> The reader should consult references 5 and 6 for more details on how to apply the wavelength increment data.

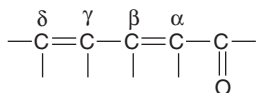
### REFERENCES

1. Woodward, R.B., Structure and the absorption spectra of  $\alpha,\beta$ -unsaturated ketones, *J. Am. Chem. Soc.*, 63, 1123, 1941.
2. Woodward, R.B., Structure and absorption spectra. III. Normal conjugated dienes, *J. Am. Chem. Soc.*, 64, 72, 1942.
3. Woodward, R.B., Structure and absorption spectra. IV. Further observations on  $\alpha,\beta$ -unsaturated ketones, *J. Am. Chem. Soc.*, 64, 76, 1942.
4. Fieser, L.F. and Fieser, M., *Natural Products Related to Phenanthrene*, Reinhold, New York, 1949.
5. Silverstein, R.M. and Webster, F.X., *Spectrometric Identification of Organic Compounds*, 6th ed., Wiley, New York, 1998.
6. Lambert, J.B., Shurvell, H.F., Lightner, D.A., Verbit, L., and Cooks, R.G., *Organic Structural Spectroscopy*, Prentice Hall, Upper Saddle River, NJ, 1998.

#### Rules of Diene Absorption

Base value for diene: 214 nm	
Increments for (each) (in nm):	
Heteroannular diene	+0
Homoannular diene	+39
Extra double bond	+30
Alkyl substituent or ring residue	+5
Exocyclic double bond	+5
Polar groups:	
–OOCR	+0
–OR	+6
–S–R	+30
Halogen	+5
–NR <sub>2</sub>	+60
$\lambda$ Calculated	= Total

### Rules for Enone Absorption<sup>a</sup>



Base value for acyclic (or six-membered) $\alpha,\beta$ -unsaturated ketone:	215 nm
Base value for five-membered $\alpha,\beta$ -unsaturated ketone:	202 nm
Base value for $\alpha,\beta$ -unsaturated aldehydes:	210 nm
Base value for $\alpha,\beta$ -unsaturated esters or carboxylic acids:	195 nm
Increments for (each) (in nm):	
Heteroannular diene	+0
Homoannular diene	+39
Double bond	+30
Alkyl groups	
$\alpha$ -	+10
$\beta$ -	+12
$\gamma$ - and higher	+18
Polar groups:	
-OH	
$\alpha$ -	+35
$\beta$ -	+30
$\delta$ -	+50
-OOCR	
$\alpha, \beta, \gamma, \delta$	+6
-OR	
$\alpha$ -	+35
$\beta$ -	+30
$\gamma$ -	+17
$\delta$ -	+31
-SR	
$\beta$ -	+85
-Cl	
$\alpha$ -	+15
$\beta$ -	+12
-Br	
$\alpha$ -	+25
$\beta$ -	+30
-NR <sub>2</sub>	
$\beta$ -	+95
Exocyclic double bond	+ 5

$\lambda$  Calculated

= Total

<sup>a</sup> Solvent corrections should be included. These are water (-8), chloroform (+1), dioxane (+5), ether (+7), hexane (+11), cyclohexane (+11). No correction for methanol or ethanol.



**Rules for Monosubstituted  
Benzene Derivatives**

Parent Chromophore (benzene): 250 nm

Substituent	Increment
-R	-4
-COR	-4
-CHO	0
-OH	-16
-OR	-16
-COOR	-16

*Note:* R is an alkyl group, and the substitution is on C<sub>6</sub>H<sub>5</sub>-.

**Rules for Disubstituted Benzene  
Derivatives**

Parent Chromophore (benzene): 250 nm

Substituent	o-	m-	p-
-R	+3	+3	+10
-COR	+3	+3	+10
-OH	+7	+7	+25
-OR	+7	+7	+25
-O <sup>-</sup>	+11	+20	+78 (variable)
-Cl	+0	+0	+10
-Br	+2	+2	+15
-NH <sub>2</sub>	+13	+13	+58
-NHCOCH <sub>3</sub>	+20	+20	+45
-NHCH <sub>3</sub>	—	—	+73
-N(CH <sub>3</sub> ) <sub>2</sub>	+20	+20	+85

*Note:* R indicates an alkyl group.

## CHAPTER 8

# Infrared Spectrophotometry

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Infrared Optics Materials  
Internal Reflectance Element Characteristics  
Water Solubility of Infrared Optics Materials  
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Mid-Range Infrared Absorptions of Major Chemical Families  
Common Spurious Infrared Absorption Bands

## INFRARED OPTICS MATERIALS

The following table lists the more common materials used for optical components (windows, prisms, etc.) in the infrared region of the electromagnetic spectrum. The properties listed are needed to choose the materials with optimal transmission characteristics.<sup>1,2</sup> The thermal properties are useful when designing experiments for operation at elevated temperatures.<sup>3-5</sup> This listing is far from exhaustive, but these are the most common materials used in instrumentation laboratories.

## REFERENCES

1. Gordon, A.J. and Ford, G.A., *The Chemist's Companion*, John Wiley & Sons, New York, 1972.
2. Willard, H.H., Dean, J.A., Settle, F.A., and Merritt, L.L., *Instrumental Methods of Analysis*, 7th ed., Wadsworth, Belmont, CA, 1995.
3. Touloukian, Y.S., Powell, R.W., Ho, C.Y., and Klemens, P.G., *Thermophysical Properties of Matter: Thermal Conductivity of Nonmetallic Solids*, Vol. 2, IF — Plenum Data Corp., New York, 1970.
4. Touloukian, Y.S., Kirby, R.K., Taylor, R.E., and Lee, T., *Thermophysical Properties of Matter: Thermal Expansion of Nonmetallic Solids*, Vol. 13, IF — Plenum Data Corp., New York, 1977.
5. Wolfe, W.L. and Zissis, G.J., Eds., *The Infrared Handbook*, Mir, Moscow, 1995.

# Infrared Optics Materials

Material	Wavelength range, $\mu\text{m}$	Wavenumber range, $\text{cm}^{-1}$	Refractive Index at 2 $\mu\text{m}$	Thermal Conductivity, $\text{w}/(\text{m}\cdot\text{K}) \times 10^2$	Thermal Expansion, $\Delta\text{L}/\text{L}$ , percent <sup>a</sup>	Notes
Sodium chloride, NaCl	0.25–16	40,000–625	1.52	7.61 (273 K) 6.61 (300 K) 4.85 (400 K)	0.448 (400 K) 0.896 (500 K)	Most common material; absorbs water; for aqueous solutions, use saturated NaCl solution as the solvent
Potassium bromide, KBr	0.25–25	40,000–400	1.53	5.00 (275 K) 4.87 (301.5 K) 4.80 (372.2 K)	0.028 (400 K) 0.429 (500 K) 0.846 (600 K)	Useful for the study of C–Br stretch region; useful for solid sample pellets
Silver chloride, AgCl	0.4–23	25,000–435	2.0	1.19 (269.8 K) 1.10 (313.0 K) 1.05 (372.5 K)	0.356 (400 K) 0.729 (500 K) 1.183 (600 K)	Not good for amines or liquids with basic nitrogen; light sensitive
Silver bromide, AgBr	0.50–35	20,000–286	2.2	0.90 (308.2 K) 0.79 (353.2 K) 0.71 (413.2 K)	0.024 (300 K) 0.109 (325 K) 0.196 (350 K)	Not good for amines or liquids with basic nitrogen; light sensitive
Calcium fluoride, $\text{CaF}_2$	0.15–9	66,700–1110	1.40	10.40 (237 K) 9.60 (309 K) 4.14 (402 K)	0.214 (400 K) 0.431 (500 K) 0.670 (600 K)	Useful for obtaining high resolution for –OH, N–H, and C–H stretching frequencies
Barium fluoride, $\text{BaF}_2$	0.20–11.5	50,000–870	1.46	11.7 (284 K) 10.9 (305 K) 10.5 (370 K)	0.233 (400 K) 0.461 (500 K) 0.698 (600 K)	Shock sensitive, should be handled with care
Cesium bromide, CsBr	1–37	10,000–270	1.67	9.24 (269.4 K) 8.00 (337.5 K) 7.76 (367.5 K)	0.526 (400 K) 1.063 (500 K) 1.645 (600 K)	Useful for C–Br stretching frequencies
Cesium iodide, CsI	1–50	10,000–200	1.74	1.15 (277.7 K) 1.05 (296.0 K) 0.95 (360.7 K)		Useful for C–Br stretching frequencies
Thallium bromide–thallium iodide, TlBr–TlI (KRS–5)	0.5–35	20,000–286	2.37		0.464 (373 K) 1.026 (473 K)	Highly toxic, handle with care; 42% TlBr, 58% TlI
Zinc selenide, ZnSe	1–18	10,000–555	2.4		0.086 (400 K) 0.175 (500 K) 0.272 (600 K)	Vacuum deposited
Germanium, Ge	0.5–11.5	20,000–870	4.0			
Silicon, Si	0.20–6.2	50,000–1613	3.5		0.033 (400 K) 0.066 (500 K) 0.102 (600 K)	
Aluminum oxide (sapphire), $\text{Al}_2\text{O}_3$	0.20–6.5	50,000–1538	1.76	25.1 (293.2 K) 21.3 (323 K) 14.2 (432.2 K)	0.075 (400 K) 0.148 (500 K) 0.225 (600 K)	
Polyethylene	16–300	625–33	1.54			Not useful for many organic compounds
Mica	200–425	50–23.5				
Fused silica, $\text{SiO}_2$	0.2–4.0	50,000–2500	1.42 (at 3 $\mu\text{m}$ )	1.38 (298 K)		Used in near infrared work; can be used with dilute and concentrated acids (except HF), not for use with aqueous alkali; metal ions can be problematic.

<sup>a</sup> Change in length divided by the starting length,  $\times 100$ .

## INTERNAL REFLECTANCE ELEMENT CHARACTERISTICS

Internal reflectance methods are a common sampling method in infrared spectrophotometry. The following table provides guidance in the selection of elements for reflectance methods.<sup>1</sup>

### REFERENCES

1. Coleman, P., *Practical Sampling Techniques for Infrared Analysis*, CRC Press, Boca Raton, FL, 1993.

**Internal Reflectance Element Characteristics**

Material	Frequency Range (cm <sup>-1</sup> )	Index of Refraction	Characteristics
Thallium iodide–thallium bromide (KRS-5)	16,000–250	2.37	Relatively soft, deforms easily; warm water, ionizable acids and bases, chlorinated solvents, and amines should not be used with this ATR element
Zinc selenide (Irtran-4)	20,000–650	2.4	Brittle; releases H <sub>2</sub> Se, a toxic material, if used with acids; water insoluble; electrochemical reactions with metal salts or complexes are possible
Zinc sulfide (Cleartran)	50,000–770	2.2	Reacts with strong oxidizing agents; relatively inert with typical aqueous, normal acids and bases and organic solvents; good thermal and mechanical shock properties; low refractive index causes spectral distortions at 45°C
Cadmium telluride (Irtran-6)	10,000–450	2.6	Expensive; relatively inert; reacts with acids
Silicon	9000–1550	3.5	Hard and brittle; useful at temperatures to 300°C; relatively inert
Germanium	5000–850	4.0	Hard and brittle; temperature opaque at 125°C
Diamond	4000–400	2.46	Extremely robust element, not brittle unless used as a composite with other materials; note that diamond absorbs at 2500–1900, thus producing a gap in the spectrum that cannot be measured.

## WATER SOLUBILITY OF INFRARED OPTICS MATERIALS

The following table provides guidance in the selection of optics materials.<sup>1</sup> Often, the solubility in (pure) water of a particular material is of critical concern.

### REFERENCES

1. Coleman, P., *Practical Sampling Techniques for Infrared Analysis*, CRC Press, Boca Raton, FL, 1993.

Water Solubility of Infrared Optics Materials		
Material	Formula	Solubility, g/100 g H <sub>2</sub> O at 20°C
Sodium chloride	NaCl	36.0
Potassium bromide	KBr	65.2
Potassium chloride	KCl	34.7
Cesium iodide	CsI	160 (at 61°C)
Fused silica	SiO <sub>2</sub>	Insoluble
Calcium fluoride	CaF <sub>2</sub>	$1.51 \times 10^{-3}$
Barium fluoride	BaF <sub>2</sub>	0.12 (at 25°C)
Thallium bromide-iodide (KRS-5)	—	$<4.76 \times 10^{-2}$
Silver bromide	AgBr	$1.2 \times 10^{-5}$
Zinc sulfide	ZnS	Insoluble
Zinc selenide (Irtan-4)	ZnSe	Insoluble
Polyethylene (high density)	—	Insoluble

## WAVELENGTH–WAVENUMBER CONVERSION TABLE

The following table provides a conversion between wavelength and wavenumber units, for use in infrared spectrophotometry.

Wavelength–Wavenumber Conversion Table										
Wave-length $\mu\text{m}$	Wavenumber ( $\text{cm}^{-1}$ )									
	0	1	2	3	4	5	6	7	8	9
2.0	5000	4975	4950	4926	4902	4878	4854	4831	4808	4785
2.1	4762	4739	4717	4695	4673	4651	4630	4608	4587	4566
2.2	4545	4525	4505	4484	4464	4444	4425	4405	4386	4367
2.3	4348	4329	4310	4292	4274	4255	4237	4219	4202	4184
2.4	4167	4149	4232	4115	4098	4082	4065	4049	4032	4016
2.5	4000	3984	3968	4953	3937	3922	3006	3891	3876	3861
2.6	3846	3831	3817	3802	3788	3774	3759	3745	3731	3717
2.7	3704	3690	3676	3663	3650	3636	3623	3610	3597	3584
2.8	3571	3559	3546	3534	3521	3509	3497	3484	3472	3460
2.9	3448	3436	3425	3413	3401	3390	3378	3367	3356	3344
3.0	3333	3322	3311	3300	3289	3279	3268	3257	3247	3236
3.1	3226	3215	3205	3195	3185	3175	3165	3155	3145	3135
3.2	3125	3115	3106	3096	3086	3077	3067	3058	3049	3040
3.3	3030	3021	3012	3003	2994	2985	2976	2967	2959	2950
3.4	2941	2933	2924	2915	2907	2899	2890	2882	2874	2865
3.5	2857	2849	2841	2833	2825	2817	2809	2801	2793	2786
3.6	2778	2770	2762	2755	2747	2740	2732	2725	2717	2710
3.7	2703	2695	2688	2681	2674	2667	2660	2653	2646	2639
3.8	2632	2625	2618	2611	2604	2597	2591	2584	2577	2571
3.9	2654	2558	2551	2545	2538	2532	2525	2519	2513	2506
4.0	2500	2494	2488	2481	2475	2469	2463	2457	2451	2445
4.1	2439	2433	2427	2421	2415	2410	2404	2398	2387	2387
4.2	2381	2375	2370	2364	2358	2353	2347	2342	2336	2331
4.3	2326	2320	2315	2309	2304	2299	2294	2288	2283	2278
4.4	2273	2268	2262	2257	2252	2247	2242	2237	2232	2227
4.5	2222	2217	2212	2208	2203	2198	2193	2188	2183	2179
4.6	2174	2169	2165	2160	2155	2151	2146	2141	2137	2132
4.7	2128	2123	2119	2114	2110	2105	2101	2096	2092	2088
4.8	2083	2079	2075	2070	2066	2062	2058	2053	2049	2045
4.9	2041	2037	2033	2028	2024	2020	2016	2012	2008	2004

Wavelength–Wavenumber Conversion Table (continued)

Wave- length $\mu\text{m}$	Wavenumber ( $\text{cm}^{-1}$ )									
	0	1	2	3	4	5	6	7	8	9
5.0	2000	1996	1992	1988	1984	1980	1976	1972	1969	1965
5.1	1961	1957	1953	1949	1946	1942	1938	1934	1931	1927
5.2	1923	1919	1916	1912	1908	1905	1901	1898	1894	1890
5.3	1887	1883	1880	1876	1873	1869	1866	1862	1859	1855
5.4	1852	1848	1845	1842	1838	1835	1832	1828	1825	1821
5.5	1818	1815	1812	1808	1805	1802	1799	1795	1792	1788
5.6	1786	1783	1779	1776	1773	1770	1767	1764	1761	1757
5.7	1754	1751	1748	1745	1742	1739	1736	1733	1730	1727
5.8	1724	1721	1718	1715	1712	1709	1706	1704	1701	1698
5.9	1695	1692	1689	1686	1684	1681	1678	1675	1672	1669
6.0	1667	1664	1661	1668	1656	1653	1650	1647	1645	1642
6.1	1639	1637	1634	1631	1629	1626	1623	1621	1618	1616
6.2	1613	1610	1608	1605	1603	1600	1597	1595	1592	1590
6.3	1587	1585	1582	1580	1577	1575	1572	1570	1567	1565
6.4	1563	1560	1558	1555	1553	1550	1548	1546	1543	1541
6.5	1538	1536	1534	1531	1529	1527	1524	1522	1520	1517
6.6	1515	1513	1511	1508	1506	1504	1502	1499	1497	1495
6.7	1493	1490	1488	1486	1484	1481	1479	1477	1475	1473
6.8	1471	1468	1466	1464	1462	1460	1458	1456	1453	1451
6.9	1449	1447	1445	1443	1441	1439	1437	1435	1433	1431
7.0	1429	1427	1425	1422	1420	1418	1416	1414	1412	1410
7.1	1408	1406	1404	1403	1401	1399	1397	1395	1393	1391
7.2	1389	1387	1385	1383	1381	1379	1377	1376	1374	1372
7.3	1370	1368	1366	1364	1362	1361	1359	1357	1355	1353
7.4	1351	1350	1348	1346	1344	1342	1340	1339	1337	1335
7.5	1333	1332	1330	1328	1326	1325	1323	1321	1319	1318
7.6	1316	1314	1312	1311	1309	1307	1305	1304	1302	1300
7.7	1299	1297	1295	1294	1292	1290	1289	1287	1285	1284
7.8	1282	1280	1279	1277	1276	1274	1272	1271	1269	1267
7.9	1266	1264	1263	1261	1259	1258	1256	1255	1253	1252
8.0	1250	1248	1247	1245	1244	1242	1241	1239	1238	1236
8.1	1235	1233	1232	1230	1229	1227	1225	1224	1222	1221
8.2	1220	1218	1217	1215	1214	1212	1211	1209	1208	1206
8.3	1205	1203	1202	1200	1199	1198	1196	1195	1193	1192
8.4	1190	1189	1188	1186	1185	1183	1182	1181	1179	1178
8.5	1176	1175	1174	1172	1171	1170	1168	1167	1166	1164
8.6	1163	1161	1160	1159	1157	1156	1155	1153	1152	1151
8.7	1149	1148	1147	1145	1144	1143	1142	1140	1139	1138
8.8	1136	1135	1134	1133	1131	1130	1129	1127	1126	1125
8.9	1124	1122	1121	1120	1119	1117	1116	1115	1114	1112



Wavelength–Wavenumber Conversion Table (continued)

Wave- length $\mu\text{m}$	Wavenumber ( $\text{cm}^{-1}$ )									
	0	1	2	3	4	5	6	7	8	9
9.0	1111	1110	1109	1107	1106	1105	1104	1103	1101	1100
9.1	1099	1098	1096	1095	1094	1093	1092	1091	1089	1088
9.2	1087	1086	1085	1083	1082	1081	1080	1079	1078	1076
9.3	1075	1074	1073	1072	1071	1070	1068	1067	1066	1065
9.4	1064	1063	1062	1060	1059	1058	1057	1056	1055	1054
9.5	1053	1052	1050	1049	1048	1047	1046	1045	1044	1043
9.6	1042	1041	1040	1038	1037	1036	1035	1034	1033	1032
9.7	1031	1030	1029	1028	1027	1026	1025	1024	1022	1021
9.8	1020	1019	1018	1017	1016	1015	1014	1013	1012	1011
9.9	1010	1009	1008	1007	1006	1005	1004	1003	1002	1001
10.0	1000	999	998	997	996	995	994	993	992	991
10.1	990	989	988	987	986	985	984	983	982	981
10.2	980	979	978	978	977	976	975	974	973	972
10.3	971	970	969	968	967	966	965	964	963	962
10.4	962	961	960	959	958	957	956	955	954	953
10.5	952	951	951	950	949	948	947	946	945	944
10.6	943	943	942	941	940	939	938	937	936	935
10.7	935	934	933	932	931	930	929	929	928	927
10.8	926	925	924	923	923	922	921	920	919	918
10.9	917	917	916	915	914	913	912	912	911	910
11.0	909	908	907	907	906	905	904	903	903	902
11.1	901	900	899	898	898	897	896	895	894	894
11.2	893	892	891	890	890	889	888	887	887	886
11.3	885	884	883	883	882	881	880	880	879	878
11.4	877	876	876	875	874	873	873	872	871	870
11.5	870	869	868	867	867	866	865	864	864	863
11.6	862	861	861	860	859	858	858	857	856	855
11.7	855	854	853	853	852	851	850	850	849	848
11.8	847	847	846	845	845	844	843	842	842	841
11.9	840	840	839	838	838	837	836	835	835	834
12.0	833	833	832	831	831	830	829	829	828	827
12.1	826	826	825	824	824	823	822	822	821	820
12.2	820	819	818	818	817	816	816	815	814	814
12.3	813	812	812	811	810	810	809	808	808	807
12.4	806	806	805	805	804	803	803	802	801	801
12.5	800	799	799	798	797	797	796	796	795	794
12.6	794	793	792	792	791	791	790	789	789	788
12.7	787	787	786	786	785	784	784	783	782	782
12.8	781	781	780	779	779	778	778	777	776	776
12.9	775	775	774	773	773	772	772	771	770	770

Wavelength–Wavenumber Conversion Table (continued)

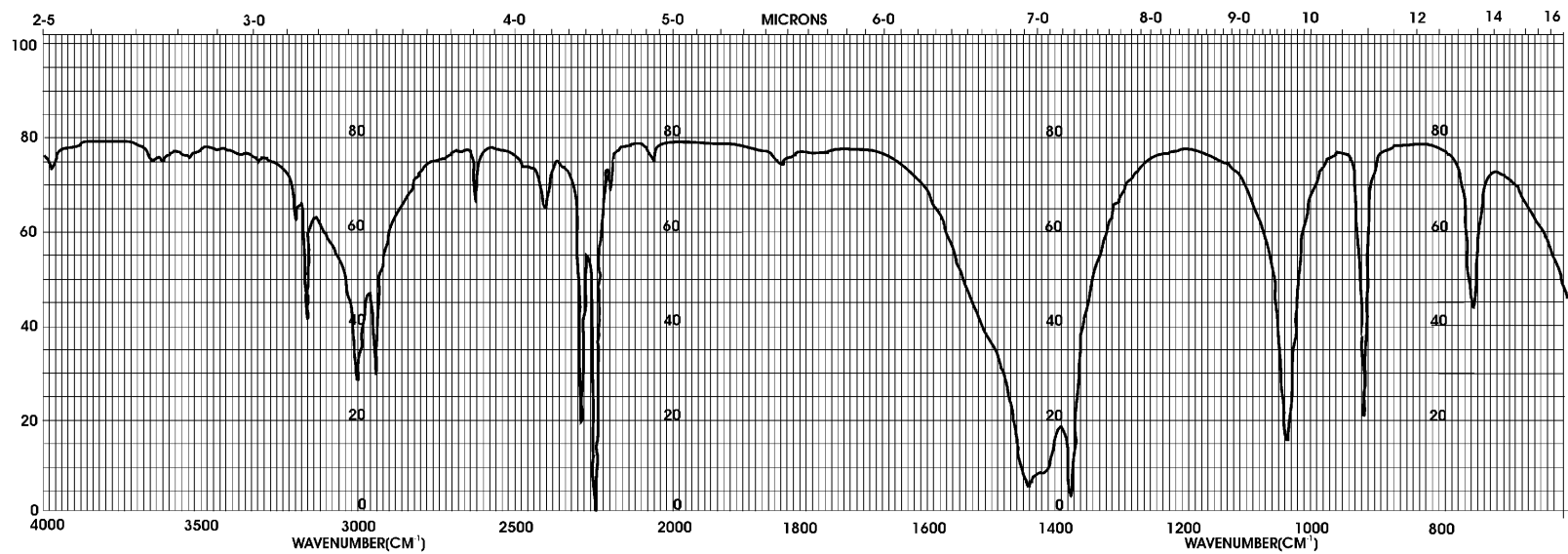
Wave- length $\mu\text{m}$	Wavenumber ( $\text{cm}^{-1}$ )									
	0	1	2	3	4	5	6	7	8	9
13.0	769	769	768	767	767	766	766	765	765	764
13.1	763	763	762	762	761	760	760	759	759	758
13.2	758	757	756	756	755	755	754	754	753	752
13.3	752	751	751	750	750	749	749	748	747	747
13.4	746	746	745	745	744	743	743	742	742	741
13.5	741	740	740	739	739	738	737	737	736	736
13.6	735	735	734	734	733	733	732	732	731	730
13.7	730	729	729	728	728	727	727	726	726	725
13.8	725	724	724	723	723	722	722	721	720	720
13.9	719	719	718	718	717	717	716	716	715	715
14.0	714	714	713	713	712	712	711	711	710	710
14.1	709	709	708	708	707	707	706	706	705	705
14.2	704	704	703	703	702	702	702	701	701	700
14.3	699	699	698	698	697	697	696	696	695	695
14.4	694	694	693	693	693	692	692	691	691	690
14.5	690	689	689	688	688	687	687	686	686	685
14.6	685	684	684	684	683	683	682	682	681	681
14.7	680	680	679	679	678	678	678	677	677	676
14.8	676	675	675	674	674	673	673	672	672	672
14.9	671	671	670	670	669	669	668	668	668	667

## USEFUL SOLVENTS FOR INFRARED SPECTROPHOTOMETRY

The following tables provide the infrared absorption spectra of several useful solvents. The spectra were measured using a double-beam spectrophotometer using a neat sample against an air reference. They are presented in both wavenumber ( $\text{cm}^{-1}$ ) and micron ( $\mu\text{m}$ ) scales. The spectra were recorded under high-concentration conditions (in terms of path length and attenuation) in order to emphasize the characteristics of each solvent. Thus, these spectra are not meant to be textbook examples of infrared spectra. The physical properties listed are those needed most often in designing spectrophotometric experiments.<sup>1-8</sup> The refractive indices are values measured with the sodium-d line. Solvation properties include the solubility parameter,  $\delta$ , hydrogen bond index,  $\lambda$ , and the solvatochromic parameters  $\alpha$ ,  $\beta$ , and  $\pi^*$ . General information and suggestions on safe handling of the solvents are provided in the notes and also in the chapter on laboratory safety in this book. The Chemical Abstract Service registry numbers are also provided for each solvent, to allow the reader to easily obtain further information using computerized database services. Note that the heat of vaporization is presented in the commonly used cal/g unit. To convert to the appropriate SI unit (J/g), multiply by 4.184. For a discussion of the units of the solubility parameter, please see the chapter dealing with supercritical fluid extraction in this book. Also relevant are the discussions of solvent stability that are presented in the chapter on HPLC and the chapter on supercritical fluid extraction.

## REFERENCES

1. Lewis, R.J., *Hawley's Condensed Chemical Dictionary*, 14th ed., John Wiley & Sons, New York, 2002.
2. Dreisbach, R.R., *Physical Properties of Chemical Compounds*, Advances in Chemistry Series 22, American Chemical Society, Washington, D.C., 1959.
3. Jamieson, D.T., Irving, J.B., and Tudhope, J.S., *Liquid Thermal Conductivity: A Data Survey to 1973*, Her Majesty's Stationary Office, Edinburgh, 1975.
4. Lewis, R.J. and Sax, N.I., *Sax's Dangerous Properties of Industrial Materials*, 9th ed., Thompson Publishing, Washington, D.C., 1995.
5. Sedivec, V. and Flek, J., *Handbook of Analysis of Organic Solvents*, John Wiley & Sons (Halsted Press), New York, 1976.
6. Epstein, W.W. and Sweat, F.W., Dimethyl sulfoxide oxidations, *Chem. Rev.*, 247, 1967.
7. Lide, D.R., Ed., *CRC Handbook for Chemistry and Physics*, 83rd ed., CRC Press, Boca Raton, FL, 2002.
8. Marcus, Y., The properties of organic liquids that are relevant to their use as solvating solvents, *Chem. Soc. Rev.*, 22, 409, 1993.



ACETONITRILE:  $\text{CH}_3\text{CN}$

### Physical Properties

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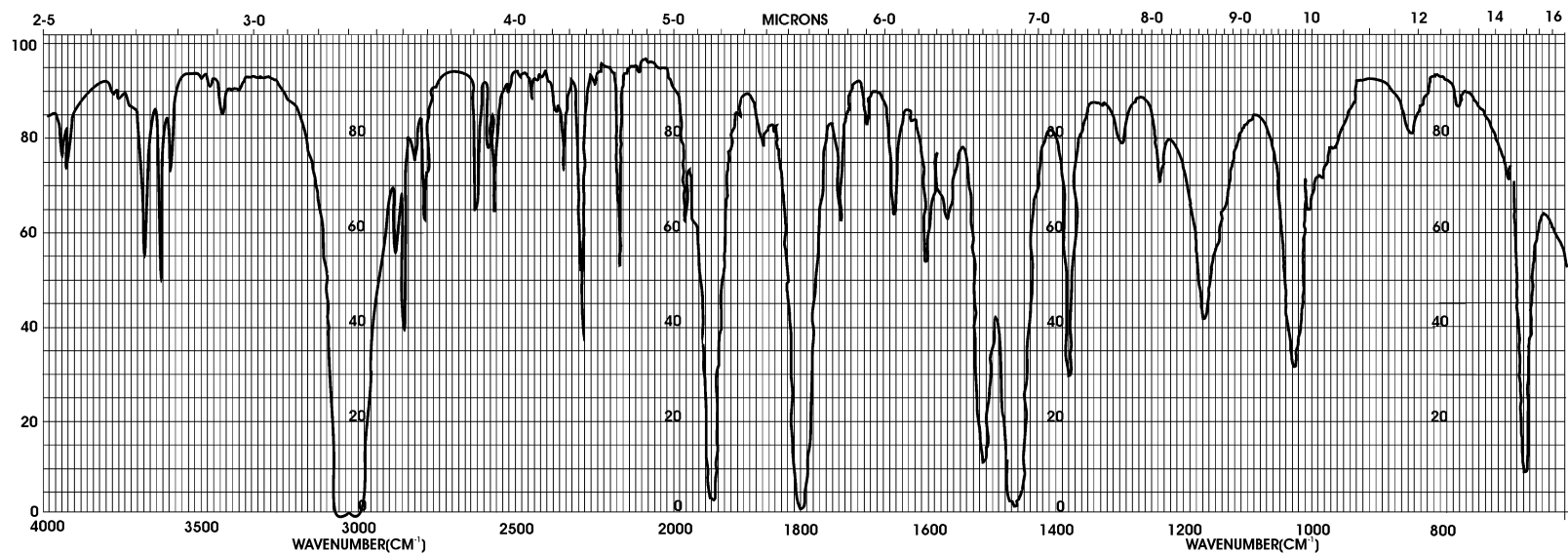
**Acetonitrile, CH<sub>3</sub>CN**

Relative molecular mass	41.05
Melting point	−45.7°C
Boiling point	81.6°C
Refractive index (20°C)	1.34423
Density (20°C)	0.7857 g/ml
Viscosity (25°C)	0.345 mPa·sec
Surface tension (20°C)	29.30 mN/m
Heat of vaporization (at boiling point)	199.1 cal/g
Thermal conductivity	0.1762 W/(m·K)
Dielectric constant (20°C)	38.8
Relative vapor density (air = 1)	1.41
Vapor pressure (20°C)	0.0097 MPa
Solubility in water <sup>a</sup>	∞
Flash point (OC)	6°C
Autoignition temperature	509°C
Explosive limits in air	4.4–16%, v/v
CAS registry number	75-05-8
Exposure limits	40 ppm, 8-h TWA
Solubility parameter, $\delta$	11.9
Solvatochromic $\alpha$	0.19
Solvatochromic $\beta$	0.40
Solvatochromic $\pi^*$	0.75

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<sup>a</sup> Forms azeotrope at 16% mass/mass that boils at 76°C.

**Note:** Highly polar solvent; sweet, ethereal odor; soluble in water; flammable, burns with a luminous flame; highly toxic by ingestion, inhalation and skin absorption; miscible with water, methanol, methyl acetate, ethyl acetate, acetone, ethers, acetamide solutions, chloroform, carbon tetrachloride, ethylene chloride, and many unsaturated hydrocarbons; immiscible with many saturated hydrocarbons (petroleum fractions); dissolves some inorganic salts such as silver nitrate, lithium nitrate, magnesium bromide; incompatible with strong oxidants; hydrolyzes in the presence of aqueous bases and strong aqueous acids. Synonyms: methyl cyanide, acetic acid nitrile, cyanomethane, ethylnitrile.



BENZENE:  $C_6H_6$

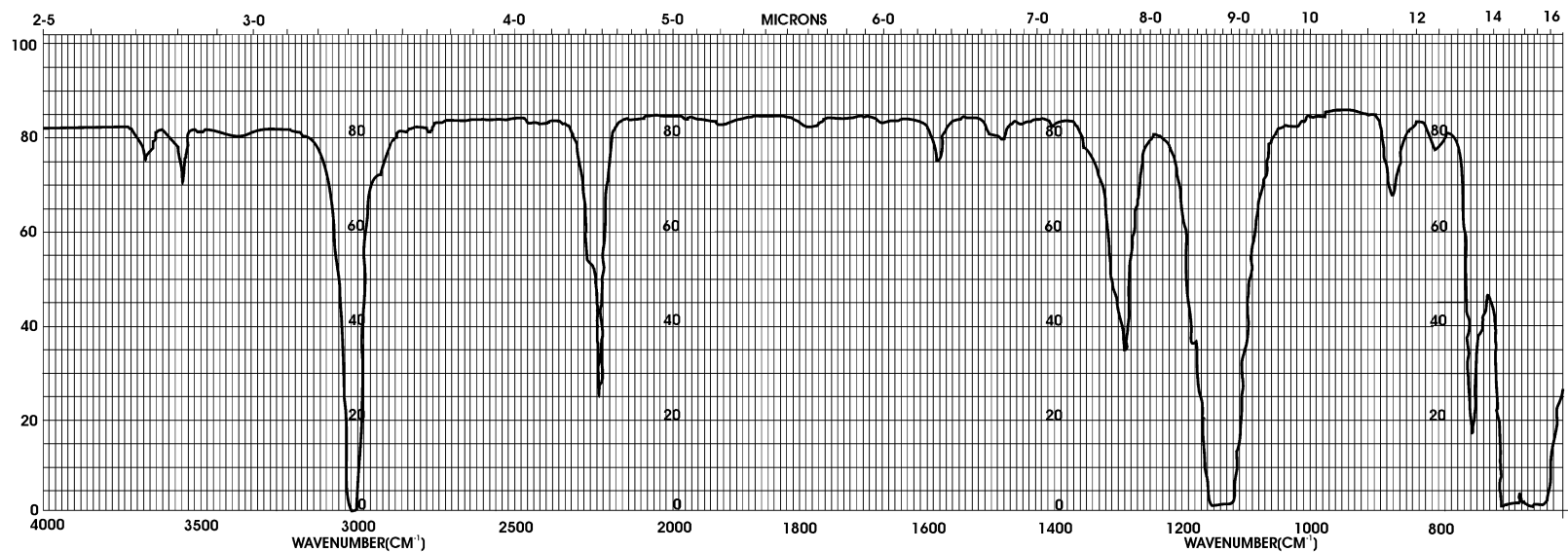
## Physical Properties

### Benzene, C<sub>6</sub>H<sub>6</sub>

Relative molecular mass	78.11
Melting point	5.5°C
Boiling point	80.1°C
Refractive index	
(20°C)	1.50110
(25°C)	1.4979
Density	
(20°C)	0.8790 g/ml
(25°C)	0.8737 g/ml
Viscosity (25°C)	0.654 mPa·sec
Surface tension (20°C)	28.87 mN/m
Heat of vaporization (at boiling point)	94.35 cal/g
Thermal conductivity (25°C)	0.1424 W/(m·K)
Dielectric constant (20°C)	2.284
Relative vapor density (air = 1)	2.77
Vapor pressure (25°C)	0.0097 MPa
Solubility in water <sup>a</sup>	0.07%, mass/mass
Flash point (OC)	–11°C
Autoignition temperature	562°C
Explosive limits in air	1.4–8.0%, v/v
CAS registry number	71-43-2
Exposure limits	10 ppm, 8-h TWA
Solubility parameter, $\delta$	9.2
Hydrogen bond index, $\lambda$	2.2
Solvatochromic $\alpha$	0.00
Solvatochromic $\beta$	0.10
Solvatochromic $\pi^*$	0.59

<sup>a</sup> Forms azeotrope (approximately 65°C).

**Note:** **Confirmed human carcinogen;** Nonpolar, aromatic solvent; sweet odor; very flammable and toxic; confirmed human carcinogen; soluble in alcohols, hydrocarbons (aliphatic and aromatic), ether, chloroform, carbon tetrachloride, carbon disulfide, slightly soluble in water; incompatible with some strong acids and oxidants, chlorine trifluoride (zinc in the presence of steam); decomposes at high temperature to form biphenyl. Synonyms: cyclohexatriene, benzin, benzol, phenylhydride. These are the most common, although there are many other synonyms.



BROMOFORM:  $\text{CHBr}_3$



### Physical Properties

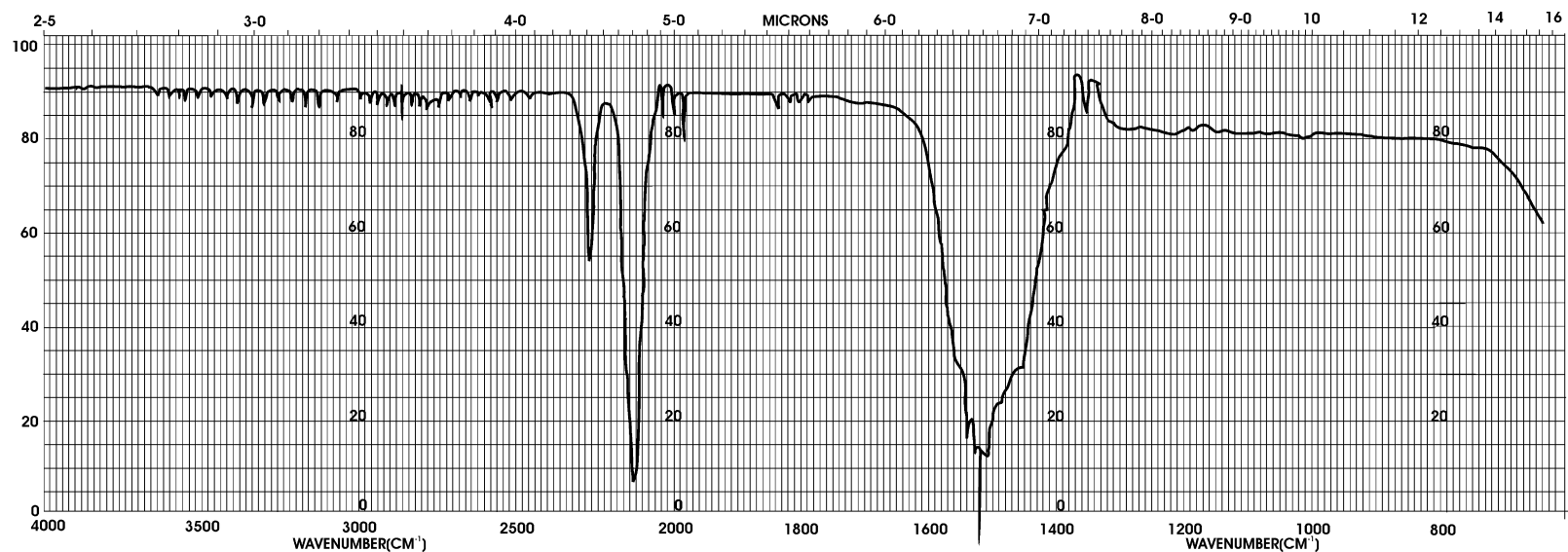
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**Bromoform, CHBr<sub>3</sub>**

Relative molecular mass	252.75
Melting point	8.3°C
Boiling point	149.5°C
Refractive index (20°C)	1.6005
Density (20°C)	2.8899 g/ml
Viscosity (25°C)	1.89 mPa·sec
Surface tension (20°C)	41.53 mN/m
Heat of vaporization (at boiling point)	38.27 cal/g
Thermal conductivity	0.0961 W/(m·K)
Dielectric constant (20°C)	4.39
Relative vapor density (air = 1)	2.77
Vapor pressure (25°C)	0.0008 MPa
Solubility in water	Slightly
Flash point (OC)	None
Autoignition temperature	None
Explosive limits in air	Nonflammable
CAS registry number	75-25-2
Exposure limits	0.5 ppm (skin)
Solvatochromic $\alpha$	0.05
Solvatochromic $\beta$	0.05
Solvatochromic $\pi^*$	0.62

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*Note:* Moderately polar, weakly hydrogen bonding solvent, heavy liquid; gradually decomposes to acquire a yellow color, air and light will accelerate this decomposition; nonflammable; commercial product is often stabilized by the addition of 3 to 4% (mass/mass) alcohols; highly toxic by ingestion, inhalation, and skin absorption; soluble in alcohols, organohalogen compounds, hydrocarbons, benzene, and many oils; incompatible with many alkali and alkaline earth metals. Synonyms: tribromomethane.



CARBON DISULFIDE: CS<sub>2</sub>

### Physical Properties

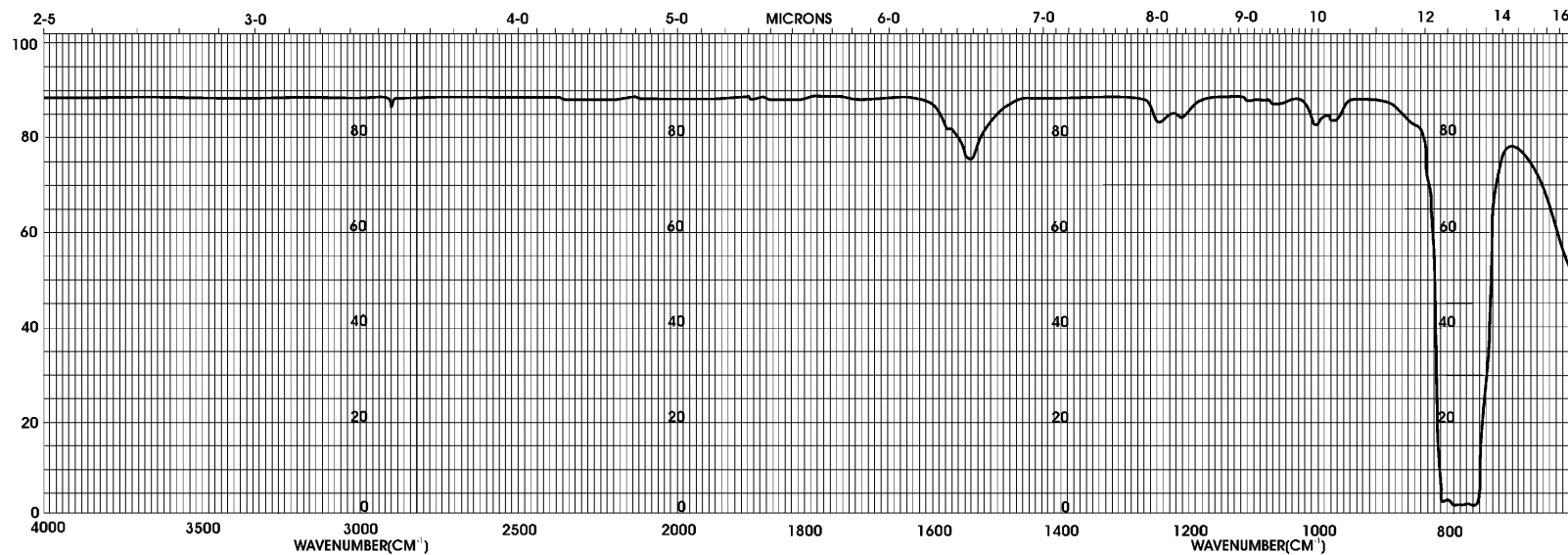
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**Carbon Disulfide, CS<sub>2</sub>**

Relative molecular mass	76.14
Melting point	−111°C
Boiling point	46.3°C
Refractive index	
(20°C)	1.6280
(25°C)	1.6232
Density	
(20°C)	1.2631 g/ml
(25°C)	1.2556 g/ml
Viscosity (20°C)	0.363 mPa·sec
Surface tension (20°C)	32.25 mN/m
Heat of vaporization (at boiling point)	84.07 cal/g
Dielectric constant (20°C)	2.641
Relative vapor density (air = 1)	2.64
Vapor pressure (25°C)	0.0448 MPa
Solubility in water (20°C)	0.29%, mass/mass
Flash point (OC)	−30°C
Autoignition temperature	100°C
Explosive limits in air	1.0–50%, v/v
CAS registry number	75-15-0
Exposure limits	20 ppm, 8-h TWA
Solvatochromic $\alpha$	0.00
Solvatochromic $\beta$	0.07
Solvatochromic $\pi^*$	0.61

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**Note:** Moderately polar solvent; soluble in alcohols, benzene, ethers, and chloroform; slightly soluble in water; very flammable and mobile; can be ignited by friction or contact with hot surfaces such as steam pipes; burns with a blue flame to produce carbon dioxide and sulfur dioxide; toxic by inhalation, ingestion, and skin absorption; strong disagreeable odor when impure; incompatible with aluminum (powder), azides, chlorine, chlorine monoxide, ethylene diamine, ethyleneamine, fluorine, nitrogen oxides, potassium, and zinc; soluble in methanol, ethanol, ethers, benzene, chloroform, carbon tetrachloride, and many oils; can be stored in metal, glass porcelain, and Teflon containers. Synonyms: carbon bisulfide, dithiocarbon anhydride.



CARBON TETRACHLORIDE: CCl<sub>4</sub>

### Physical Properties

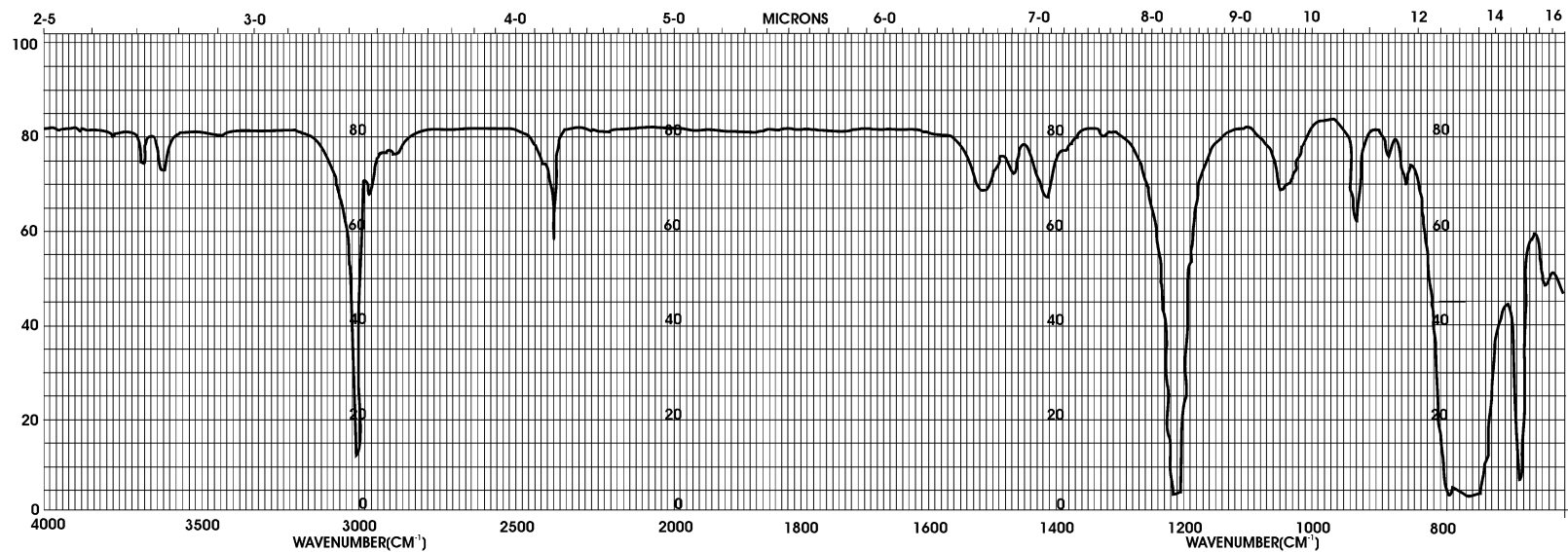
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**Carbon Tetrachloride, CCl<sub>4</sub>**

Relative molecular mass	153.82
Melting point	−23.0°C
Boiling point	76.74°C
Refractive index	
(20°C)	1.4607
(25°C)	1.4570
Density	
(20°C)	1.5940 g/ml
(25°C)	1.5843 g/ml
Viscosity (20°C)	0.969 mPa·sec
Surface tension (20°C)	26.75 mN/m
Heat of vaporization (at boiling point)	46.8 cal/g
Thermal conductivity (20°C)	0.1070 W/(m·K)
Dielectric constant (20°C)	2.238
Relative vapor density (air = 1)	5.32
Vapor pressure (25°C)	0.0122 MPa
Solubility in water (20°C)	0.08, w/w
Flash point (OC)	Incombustible
Autoignition temperature	Incombustible
Explosive limits in air	Nonexplosive
CAS registry number	56-23-5
Exposure limits	5 ppm (skin)
Solubility parameter, $\delta$	8.6
Hydrogen bond index, $\lambda$	2.2
Solvatochromic $\alpha$	0.00
Solvatochromic $\beta$	0.10
Solvatochromic $\pi^*$	0.28

---

*Note:* Nonpolar solvent; soluble in alcohols, ethers, chloroform, benzene, and most fixed and volatile oils; insoluble in water; nonflammable; extremely toxic by inhalation, ingestion, or skin absorption; carcinogenic; incompatible with allyl alcohol, silanes, triethyldialuminum, and many metals (e.g., sodium). Synonyms: tetrachloromethane, perchloromethane, methane tetrachloride, Halon-104.



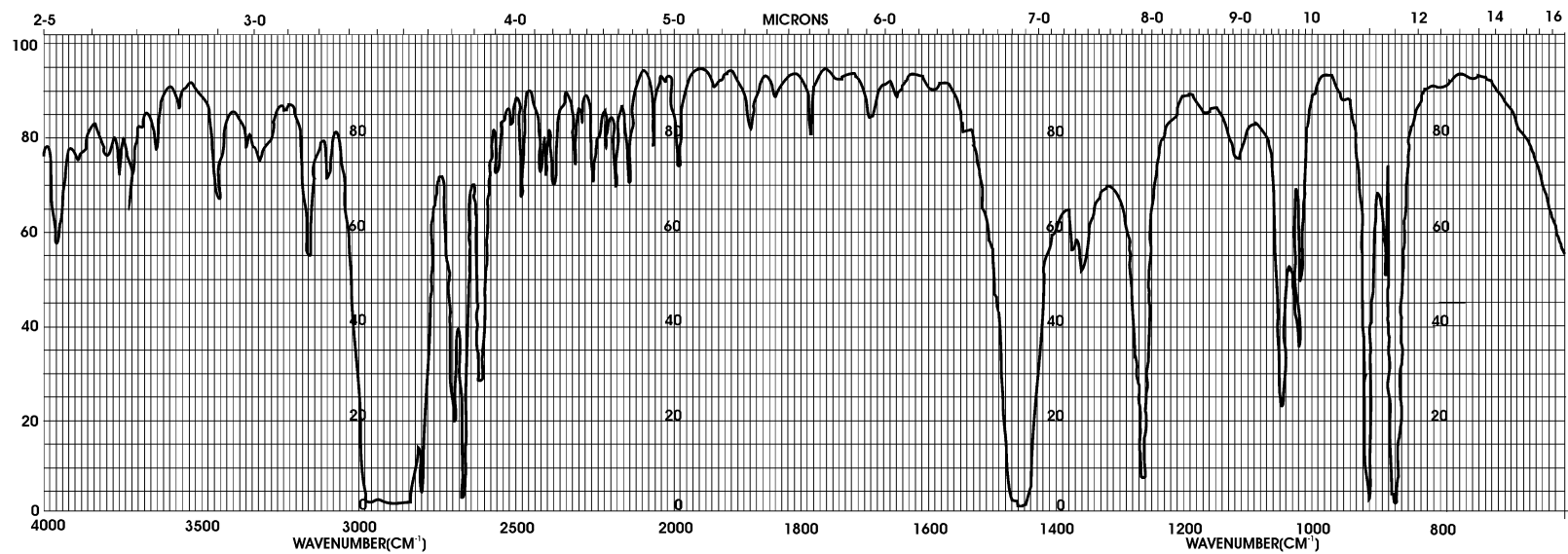
CHLOROFORM:  $\text{CHCl}_3$

### Physical Properties

<b>Chloroform, CHCl<sub>3</sub></b>	
Relative molecular mass	119.38
Melting point	−63.2°C
Boiling point	61.2°C
Refractive index	
(20°C)	1.4458
(25°C)	1.4422
Density	
(20°C)	1.4892 g/ml
(25°C)	1.4798 g/ml
Viscosity (20°C)	0.566 mPa·sec
Surface tension	27.2 mN/m
Heat of vaporization (at boiling point)	59.3 cal/g
Thermal conductivity (20°C)	0.1164 W/(m·K)
Dielectric constant (20°C)	4.806
Relative vapor density (air = 1)	4.13
Vapor pressure (25°C)	0.0263 MPa
Solubility in water	0.815%, w/w
Flash point (OC)	Incombustible <sup>a</sup>
Autoignition temperature	Incombustible <sup>a</sup>
Explosive limits in air	Nonexplosive
CAS registry number	67-66-3
Exposure limits	10 ppm, 8-h TWA
Solubility parameter, $\delta$	9.3
Hydrogen bond index, $\lambda$	2.2
Solvatochromic $\alpha$	0.20
Solvatochromic $\beta$	0.10
Solvatochromic $\pi^*$	0.58

<sup>a</sup> Although chloroform is nonflammable, it will burn upon prolonged exposure to flame or high temperature.

**Note:** Polar solvent; soluble in alcohols, ether, benzene, and most oils; usually stabilized with methanol to prevent phosgene formation; flammable and highly toxic by inhalation, ingestion, or skin absorption; narcotic; carcinogenic; incompatible with caustics, active metals, aluminum powder, potassium, sodium, magnesium. Synonyms: trichloromethane, methane trichloride.



CYCLOHEXANE:  $C_6H_{12}$



### Physical Properties

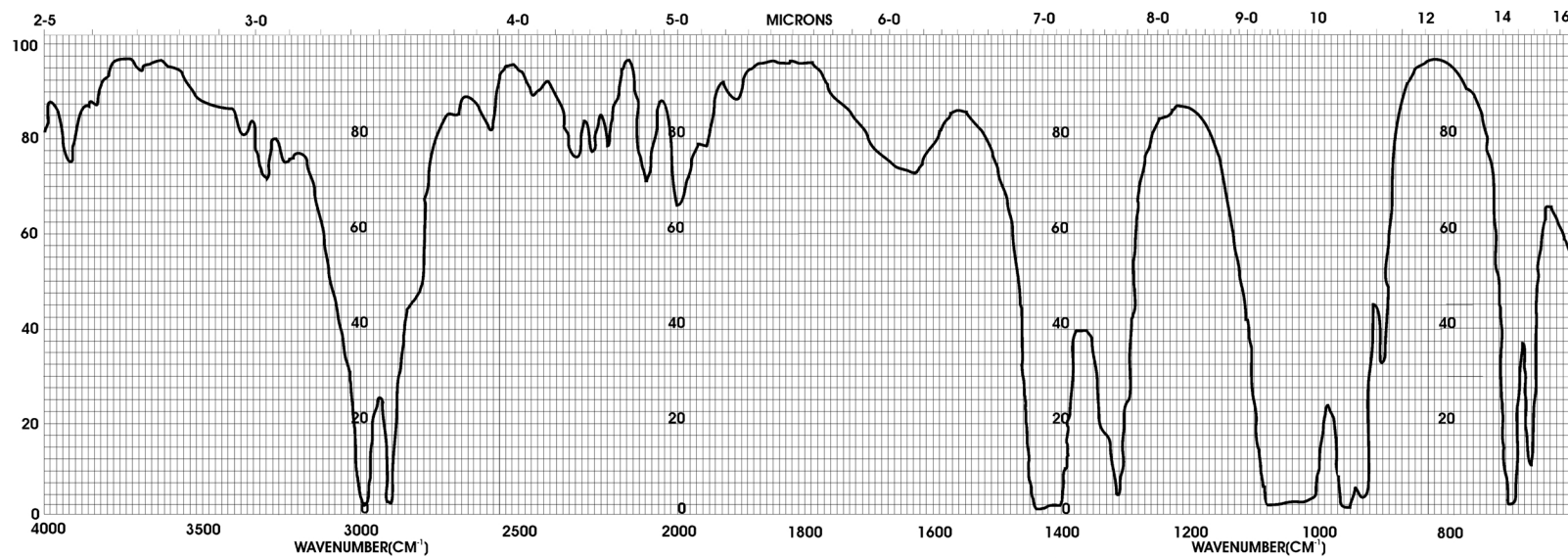
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**Cyclohexane, C<sub>6</sub>H<sub>12</sub>**

Relative molecular mass	84.16
Melting point	6.3°C
Boiling point	80.7°C
Refractive index	
(20°C)	1.4263
(25°C)	1.4235
Density	
(20°C)	0.7786 g/ml
(25°C)	0.7739 g/ml
Viscosity (20°C)	1.06 mPa·sec
Surface tension (20°C)	24.99 mN/m
Heat of vaporization (at boiling point)	85.62 cal/g
Thermal conductivity (20°C)	0.122 W/(m·K)
Dielectric constant (20°C)	2.023
Relative vapor density (air = 1)	2.90
Vapor pressure (25°C)	0.0111 MPa
Solubility in water (20°C)	<0.01%, mass/mass
Flash point (OC)	-17°C
Autoignition temperature	245°C
Explosive limits in air	1.31–8.35%, v/v
CAS registry number	110-82-7
Exposure limits	330 ppm, 8-h TWA
Solvatochromic $\alpha$	0.00
Solvatochromic $\beta$	0.00
Solvatochromic $\pi^*$	0.00

---

**Note:** Nonpolar hydrocarbon solvent; mild, gasoline-like odor; soluble in hydrocarbons, alcohols, organic halides, acetone, benzene; flammable; moderately toxic by inhalation, ingestion, or skin absorption, may be narcotic at high concentrations; reacts with oxygen (air) at elevated temperatures; decomposes upon heating; incompatible with strong oxidants. Synonyms: benzene hexahydride, hexamethylene, hexanaphthene, hexahydrobenzene.



DIMETHYL SULFOXIDE:  $(\text{CH}_3)_2\text{SO}$

### Physical Properties

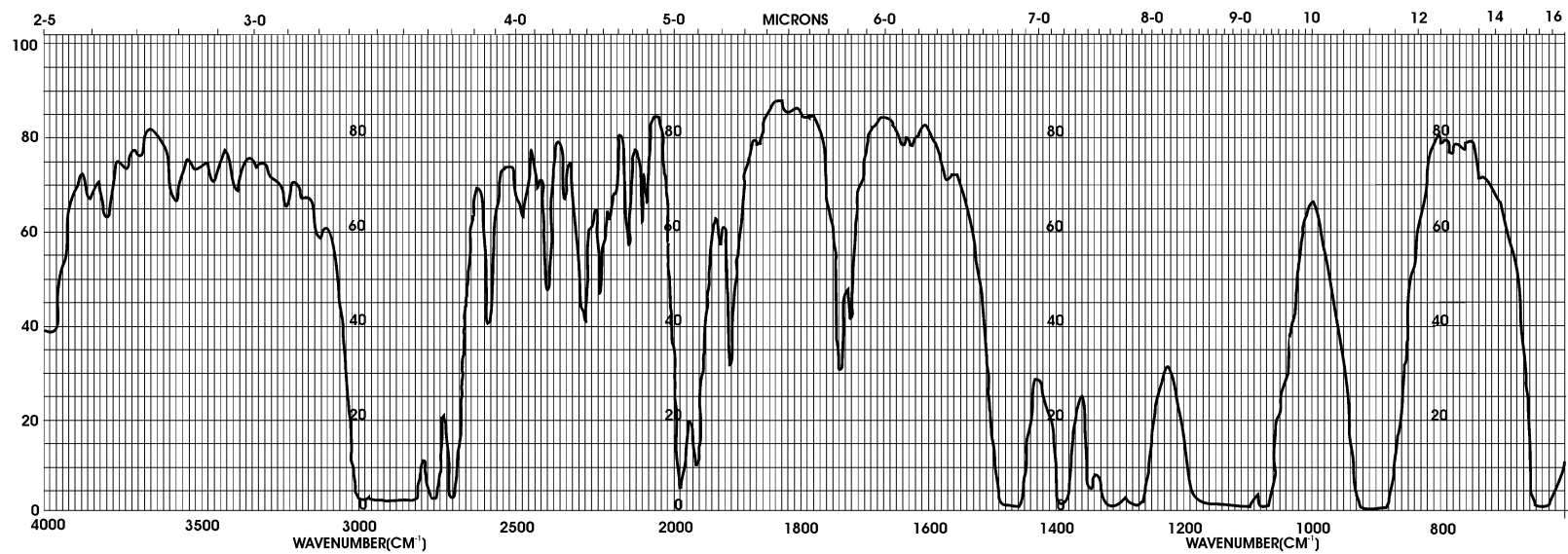
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**Dimethyl Sulfoxide, (CH<sub>3</sub>)<sub>2</sub>SO**

Relative molecular mass	78.13
Melting point	18.5°C
Boiling point	189°C
Refractive index (20°C)	1.4770
Density (20°C)	1.1014 g/ml
Viscosity (25°C)	1.98 mPa·sec
Surface tension	43.5 mN/m
Heat of vaporization (at boiling point)	144 cal/g
Relative vapor density (air = 1)	2.7
Vapor pressure	$5.3 \times 10^{-5}$ MPa
Solubility in water	$\infty$
Flash point (OC)	95°C
Autoignition temperature	215°C
Explosive limits in air	26.0–28.5%, v/v
CAS registry number	67-68-5
Exposure limits	None established
Solubility parameter, $\delta$	13.0
Hydrogen bond index, $\lambda$	5.0
Solvatochromic $\alpha$	0.00
Solvatochromic $\beta$	0.76
Solvatochromic $\pi^*$	1.00

---

*Note:* Colorless, odorless (when pure), hygroscopic liquid, powerful aprotic solvent; dissolves many inorganic salts, soluble in water; combustible; readily penetrates the skin; incompatible with strong oxidizers and many halogenated compounds (e.g., alkyl halides, aryl halides), oxygen, peroxides, diborane, perchlorates. Synonyms: DMSO, methyl sulfoxide, sulfinylbismethane.



### Physical Properties

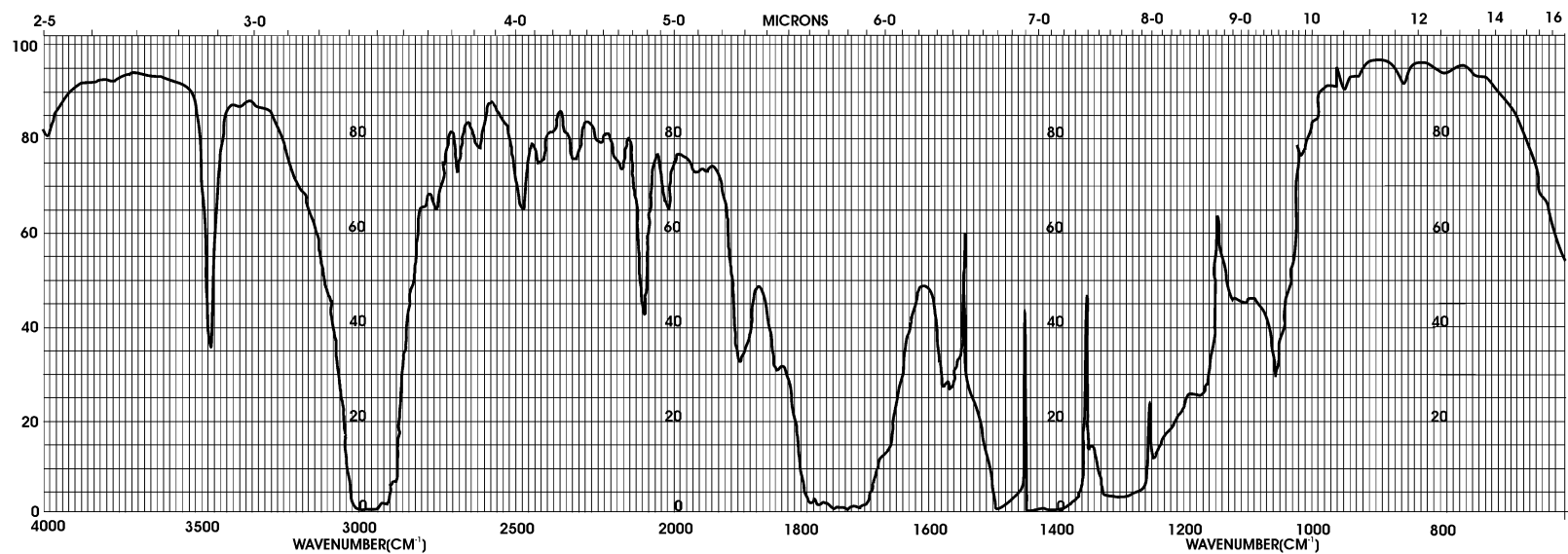
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**1,4-Dioxane, OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>**

Relative molecular mass	88.11
Melting point	11°C
Boiling point	101.3°C
Refractive index	
(20°C)	1.4221
(25°C)	1.4195
Density	
(20°C)	1.0338 g/ml
(25°C)	1.0282 g/ml
Viscosity (20°C)	1.37 mPa·sec
Surface tension (20°C)	33.74 mN/m
Heat of vaporization (at boiling point)	98 cal/g
Dielectric constant (20°C)	2.209
Relative vapor density (air = 1)	3.03
Vapor pressure (25°C)	0.0053 MPa
Solubility in water	∞
Flash point (OC)	12°C
Autoignition temperature	180°C
Explosive limits in air	1.97–22.2%, v/v
CAS registry number	123-91-1
Exposure limits	100 ppm (skin)
Solubility parameter, $\delta$	9.9
Hydrogen bond index, $\lambda$	5.7
Solvatochromic $\alpha$	0.00
Solvatochromic $\beta$	0.37
Solvatochromic $\pi^*$	0.55

---

*Note:* Moderately polar solvent; soluble in water and most organic solvents; flammable; highly toxic by ingestion and inhalation; absorbed through the skin; may cause central nervous system depression, necrosis of the liver and kidneys; incompatible with strong oxidizers. Synonyms: diethylene ether, 1,4-diethylene dioxide, diethylene dioxide, dioxethylene ether.



ETHYL ACETATE:  $\text{CH}_3\text{COOC}_2\text{H}_5$

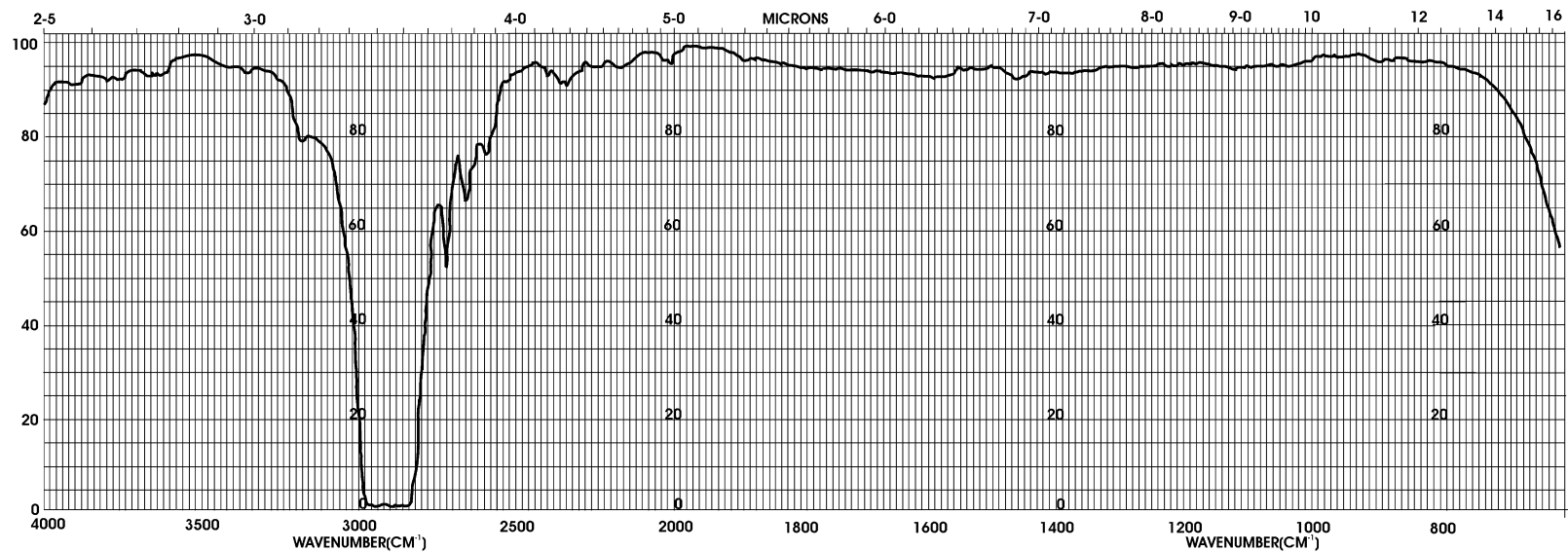
### Physical Properties

#### Ethyl Acetate, $\text{CH}_3\text{COOC}_2\text{H}_5$

Relative molecular mass	88.11
Melting point	-83.58°C
Boiling point	77.06°C
Refractive index	
(20°C)	1.3723
(25°C)	1.3698
Density	
(20°C)	0.9006 g/ml
(25°C)	0.8946 g/ml
Viscosity (20°C)	0.452 mPa·sec
Surface tension (20°C)	23.95 mN/m
Heat of vaporization (at boiling point)	87.63 cal/g
Thermal conductivity	0.122 W/(m·K)
Dielectric constant (25°C)	6.02
Relative vapor density (air = 1)	3.04
Vapor pressure (20°C)	0.0097 MPa
Solubility in water (20°C) <sup>a</sup>	3.3%, mass/mass
Flash point (OC)	-1°C
Autoignition temperature	486°C
Explosive limits in air	2.18–11.5%, v/v
CAS registry number	141-78-6
Exposure limits	440 ppm, 8-h TWA
Solubility parameter, $\delta$	9.1
Hydrogen bond index, $\lambda$	5.2
Solvatochromic $\alpha$	0.00
Solvatochromic $\beta$	0.43
Solvatochromic $\pi^*$	0.55

<sup>a</sup> Forms an azeotrope with water at 6.1%, mass/mass, that boils at 70.4°C.

**Note:** Polar solvent; soluble in water, alcohols (organic halides), ether, and many oils; flammable; moderately toxic by inhalation and skin absorption; incompatible with strong oxidizers, nitrates, strong alkalis, strong acids. Synonyms: acedin, acetic ether, acetic ester, ethyl ethanoate, vinegar naphtha, acetic acid ethyl ester.



*n*-HEXANE:  $\text{CH}_3(\text{CH}_2)_4\text{CH}_3$

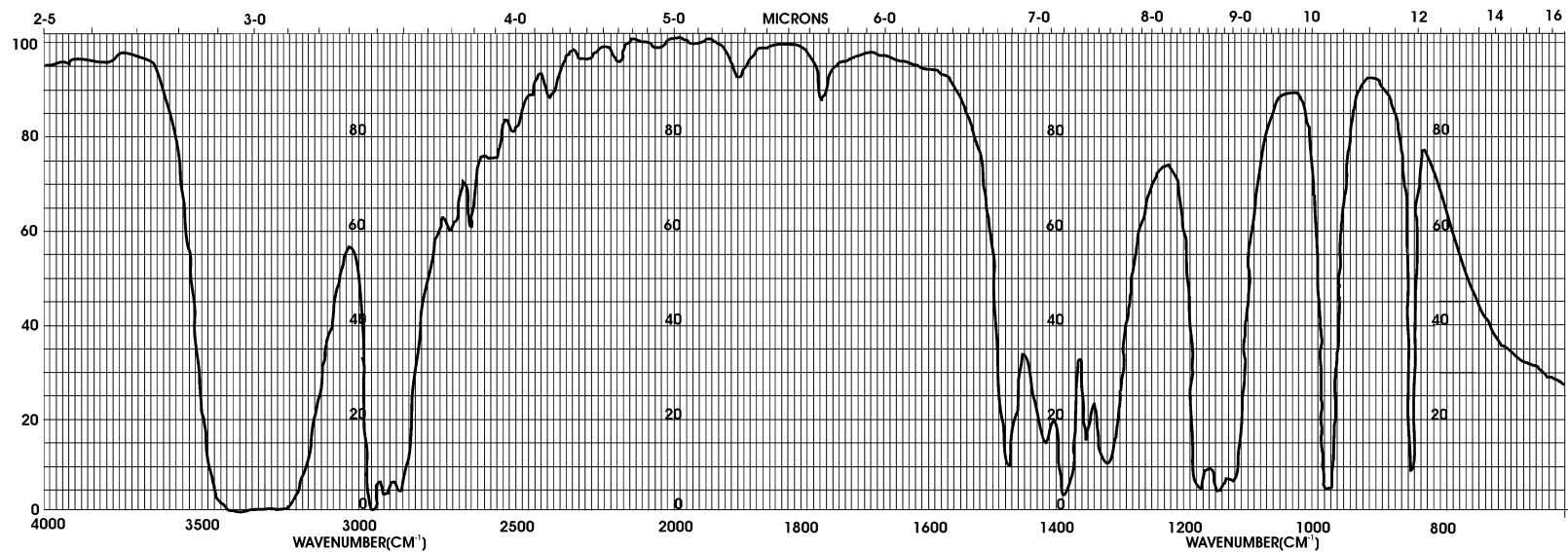


### Physical Properties

#### ***n*-Hexane, CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>**

Relative molecular mass	86.18
Melting point	−95°C
Boiling point	68.742°C
Refractive index	
(20°C)	1.37486
(25°C)	1.3723
Density	
(20°C)	0.6594 g/ml
(25°C)	0.6548 g/ml
Viscosity (20°C)	0.31 mPa·sec
Surface tension (20°C)	18.42 mN/m
Heat of vaporization (at boiling point)	80.03 cal/g
Thermal conductivity (20°C)	0.1217 W/(m·K)
Dielectric constant (20°C)	1.890
Relative vapor density (air = 1)	2.97
Vapor pressure (25°C)	0.0222 MPa
Solubility in water (20°C)	0.011%, mass/mass
Flash point (OC)	−26°C
Autoignition temperature	247°C
Explosive limits in air	1.25–6.90%, v/v
CAS registry number	110-54-3
Exposure limits	500 ppm, 8-h TWA
Solubility parameter, $\delta$	9.3
Hydrogen bond index, $\lambda$	2.2
Solvatochromic $\alpha$	0.00
Solvatochromic $\beta$	0.00
Solvatochromic $\pi^*$	0.08

**Note:** Nonpolar solvent; soluble in alcohols, hydrocarbons, organic halides, acetone, and ethers; insoluble in water; flammable; moderately toxic by inhalation and ingestion; incompatible with strong oxidizers. Synonyms: hexane, hexyl hydride.



ISOPROPANOL:  $(\text{CH}_3)_2\text{CHOH}$

### Physical Properties

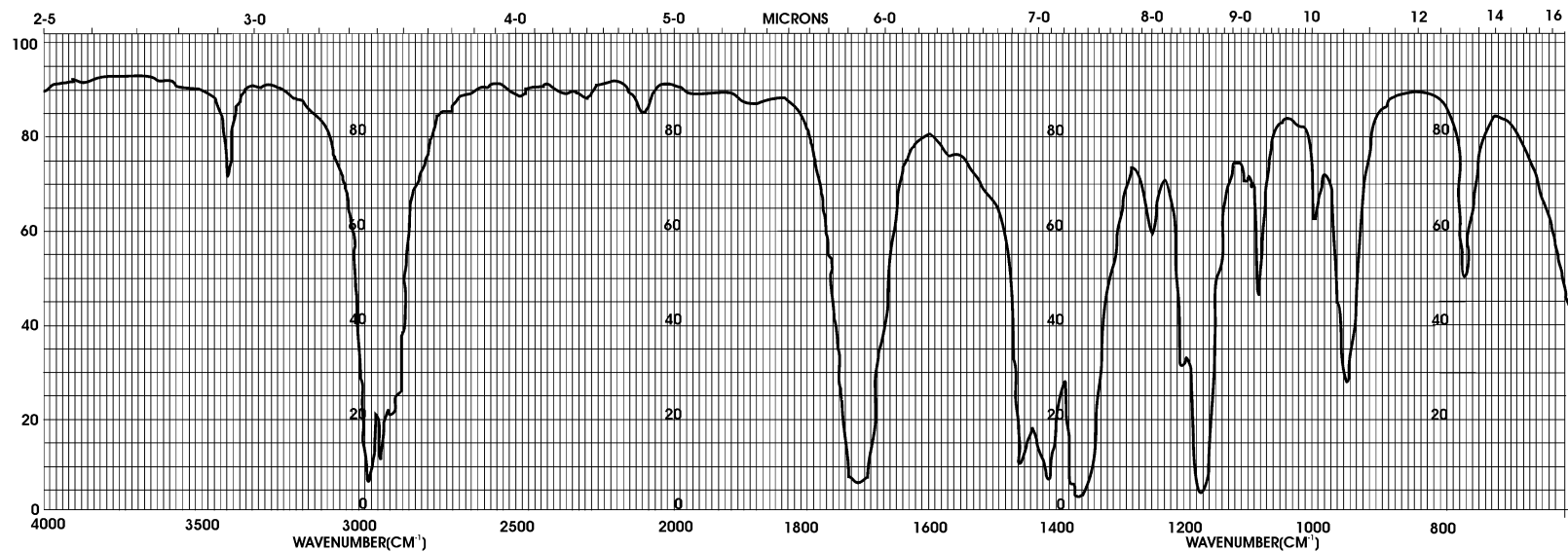
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**Isopropanol, (CH<sub>3</sub>)<sub>2</sub>CHOH**

Relative molecular mass	60.10
Melting point	89.8°C
Boiling point	82.4°C
Refractive index	
(20°C)	1.3771
(25°C)	1.3750
Density	
(20°C)	0.7864 g/ml
(25°C)	0.7812 g/ml
Viscosity (20°C)	2.43 mPa·sec
Surface tension (20°C)	21.99 mN/m
Heat of vaporization (at boiling point)	160 cal/g
Dielectric constant (25°C)	18.3
Relative vapor density (air = 1)	2.07
Vapor pressure	0.0044 MPa
Solubility in water (20°C)	∞
Flash point (OC)	16°C
Autoignition temperature	456°C
Explosive limits in air	2.02–11.8%, v/v
CAS registry number	67-63-0
Exposure limits	400 ppm (skin)
Solubility parameter, $\delta$	11.5
Hydrogen bond index, $\lambda$	8.9
Solvatochromic $\alpha$	0.76
Solvatochromic $\beta$	0.84
Solvatochromic $\pi^*$	0.48

---

*Note:* Polar solvent; soluble in water, alcohols, ethers, many hydrocarbons, and oils; flammable and moderately toxic by ingestion, inhalation, and skin absorption; incompatible with strong oxidizers. Synonyms: dimethyl carbinol, *sec*-propyl alcohol, 2-propanol, isopropyl alcohol.



METHYL ETHYL KETONE:  $\text{CH}_3\text{COC}_2\text{H}_5$

### Physical Properties

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**Methyl Ethyl Ketone, CH<sub>3</sub>COC<sub>2</sub>H<sub>5</sub>**

Relative molecular mass	72.11
Melting point	-86.4°C
Boiling point	79.6°C
Refractive index	
(20°C)	1.379
(25°C)	1.3761
Density	
(20°C)	0.8054 g/ml
(25°C)	0.8002 g/ml
Viscosity (20°C)	0.448 mPa·sec
Surface tension (20°C)	24.50 mN/m
Heat of vaporization (at boiling point)	108.74 cal/g
Thermal conductivity	0.1465 W/(m·K)
Dielectric constant (20°C)	18.5
Relative vapor density (air = 1)	2.41
Vapor pressure (25°C)	0.0129 MPa
Solubility in water (20°C)	27.33%, mass/mass
Flash point (OC)	2°C
Autoignition temperature	516°C
Explosive limits in air	1.81–11.5%, v/v
CAS registry number	78-93-3
Exposure limits	200 ppm, 8-h TWA
Solubility parameter, $\delta$	9.3
Hydrogen bond index, $\lambda$	5.0
Solvatochromic $\alpha$	0.6
Solvatochromic $\beta$	0.48
Solvatochromic $\pi^*$	0.67

---

*Note:* Polar solvent; soluble in water, ketones, organic halides, alcohols, ether, and many oils; highly flammable; narcotic by inhalation; incompatible with strong oxidizers, nitrates, nitric acid, reducing agents. Synonyms: ethyl methyl ketone, 2-butanone, MEK, methyl acetone.



*n*-OCTANE:  $\text{CH}_3(\text{CH}_2)_6\text{CH}_3$

### Physical Properties

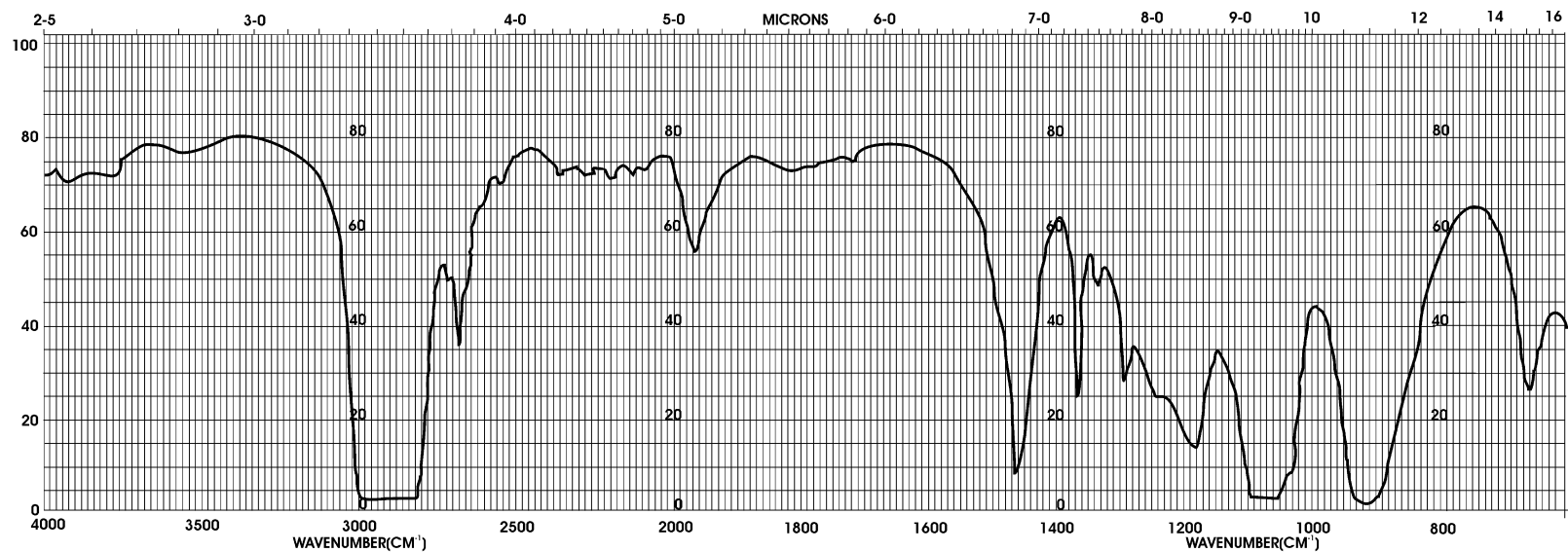
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***n*-Octane, CH<sub>3</sub>(CH<sub>2</sub>)<sub>6</sub>CH<sub>3</sub>**

Relative molecular mass	114.23
Melting point	−56.667°C
Boiling point	125.667°C
Refractive index	
(20°C)	1.39745
(25°C)	1.3951
Density	
(20°C)	0.7025 g/ml
(25°C)	0.6985 g/ml
Viscosity (20°C)	0.539 mPa·sec
Surface tension (20°C)	21.75 mN/m
Heat of vaporization (at boiling point)	73.3 cal/g
Dielectric constant (20°C)	1.948
Relative vapor density (air = 1)	3.86
Vapor pressure (25°C)	0.0023 MPa
Solubility in water (20°C)	~0.002%, mass/mass
Flash point (CC)	13°C
Autoignition temperature	232°C
Explosive limits in air	0.84–3.2%, v/v
CAS registry number	111-65-9
Exposure limits	550 ppm, 8-h TWA
Hydrogen bond index, $\lambda$	2.2
Solvatochromic $\alpha$	0.00
Solvatochromic $\beta$	0.00
Solvatochromic $\pi^*$	0.01

---

*Note:* Nonpolar solvent; soluble in alcohol, acetone, and hydrocarbons; insoluble in water; flammable; incompatible with strong oxidizers. Synonyms: octane.



TETRAHYDROFURAN:  $\text{CH}_2(\text{CH}_2)_2\text{CH}_2\text{O}$



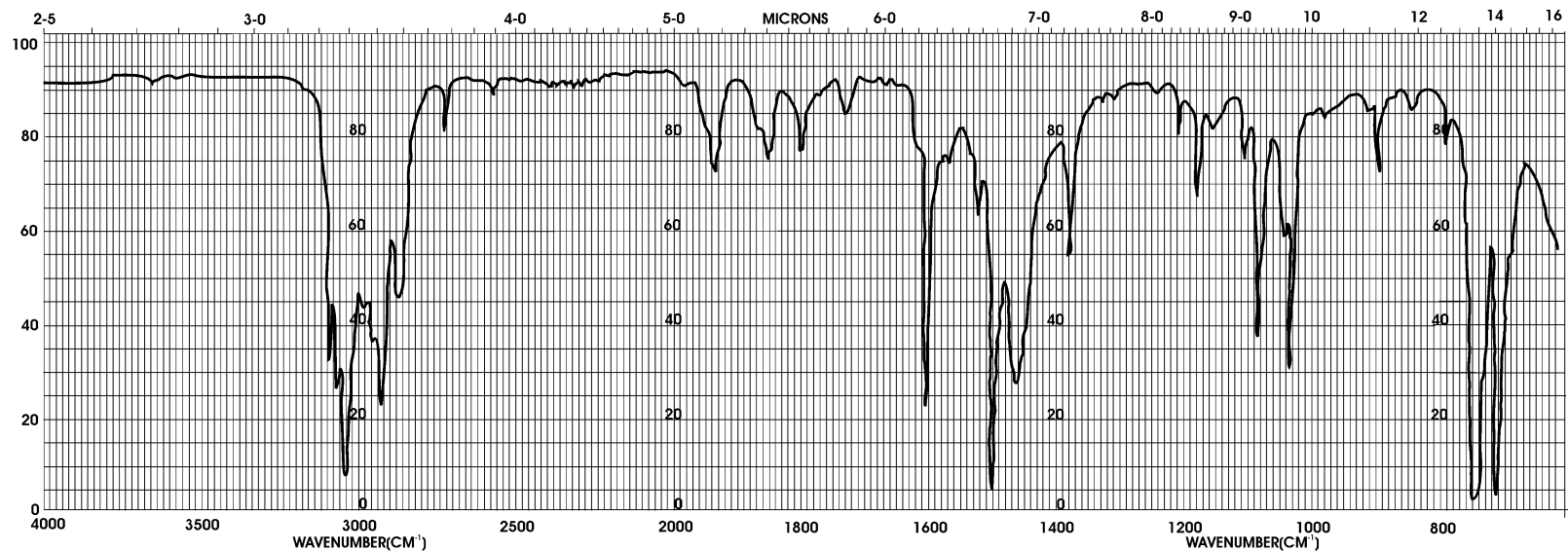
### Physical Properties

#### Tetrahydrofuran, CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>O

Relative molecular mass	72.108
Melting point	−65°C
Boiling point	66°C
Refractive index	
(20°C)	1.4070
(25°C)	1.4040
Density	
(20°C)	0.8880 g/ml
(25°C)	0.8818 g/ml
Viscosity (20°C)	0.55 mPa·sec
Surface tension (20°C)	26.4 mN/m
Heat of vaporization (at boiling point)	95 cal/g
Dielectric constant (20°C)	7.54
Relative vapor density (air = 1)	2.5
Vapor pressure (20°C)	0.0191 MPa, 143 mmHg
Solubility in water (20°C) <sup>a</sup>	∞
Flash point (CC)	−17°C
Autoignition temperature	260°C
Explosive limits in air	1.8–11.8%, v/v
CAS registry number	109-99-9
Exposure limits	200 ppm, 8-h TWA
Solubility parameter, δ	9.1
Hydrogen bond index, λ	5.3
Solvatochromic α	0.00
Solvatochromic β	0.55
Solvatochromic π*	0.58

<sup>a</sup> pH of aqueous solution = 7.

**Note:** Moderately polar solvent, ethereal odor; soluble in water and most organic solvents; flammable; moderately toxic; incompatible with strong oxidizers; can form potentially explosive peroxides upon long standing in air; see the relevant tables in the chapter on laboratory safety; commercially, it is often stabilized against peroxidation with 0.5 to 1.0% (mass/mass) *p*-cresol, 0.5 to 1.0% (mass/mass) hydroquinone, or 0.01% (mass/mass) 4,4'-thiobis(6-*tert*-butyl-*m*-cresol); can polymerize in the presence of cationic initiators such as Lewis acids or strong proton acids. Synonyms: THF, tetramethylene oxide, diethylene oxide, 1,4-epoxybutane, oxolane, oxacyclopentane.



TOLUENE:  $\text{CH}_3\text{C}_6\text{H}_5$

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**Physical Properties**

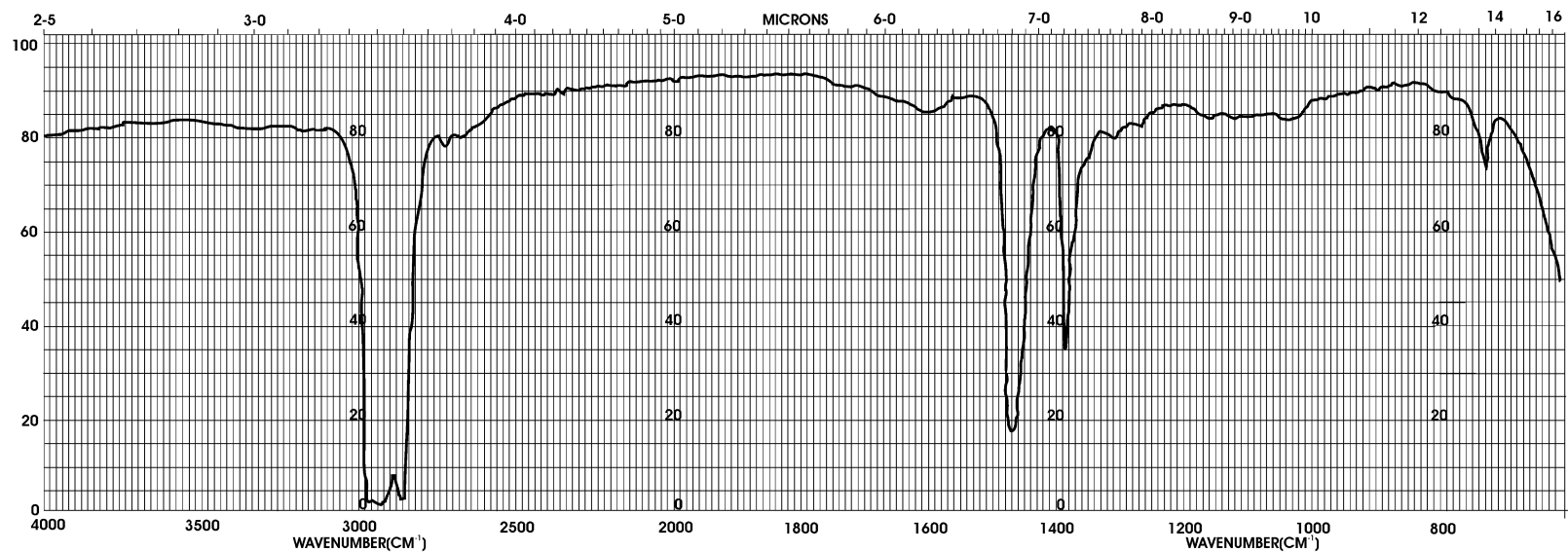
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**Toluene, CH<sub>3</sub>C<sub>6</sub>H<sub>5</sub>**

Relative molecular mass	92.14
Melting point	−94.5°C
Boiling point	110.7°C
Refractive index	
(20°C)	1.497
(25°C)	1.4941
Density	
(20°C)	0.8669 g/ml
(25°C)	0.8623 g/ml
Viscosity (20°C)	0.587 mPa·sec
Surface tension (20°C)	28.52 mN/m
Heat of vaporization (at boiling point)	86.50 cal/g
Thermal conductivity (20°C)	0.1348 W/(m·K)
Dielectric constant (25°C)	2.379
Relative vapor density (air = 1)	3.14
Vapor pressure (25°C)	0.0036 MPa
Solubility in water	0.047%, mass/mass
Flash point (CC)	4°C
Autoignition temperature	552°C
Explosive limits in air	1.27–1.0%, v/v
CAS registry number	108-88-3
Exposure limits	200 ppm, 8-h TWA
Solubility parameter, $\delta$	8.9
Hydrogen bond index, $\lambda$	3.8
Solvatochromic $\alpha$	0.00
Solvatochromic $\beta$	0.11
Solvatochromic $\pi^*$	0.54

---

*Note:* Aromatic solvent; sweet pungent odor; soluble in benzene, alcohols, organic halides, ethers; insoluble in water; highly flammable; toxic by ingestion, inhalation, and absorption through the skin, narcotic at high concentrations; incompatible with strong oxidants; decomposes under high heat to form (predominantly) dimethylbiphenyl. Synonyms: toluol, methylbenzene, methylbenzol, phenylmethane.



PARAFFIN OIL

### Physical Properties

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#### Paraffin Oil

Relative molecular mass	Variable
Melting point	−20°C (approximate)
Boiling point	315°C (approximate)
Refractive index	
(20°C)	1.4720
(25°C)	1.4697
Solubility in water	Insoluble
Flash point (OC)	229°C
Explosive limits in air	0.6–6.5%, v/v
CAS registry number	8012-95-1
Exposure limits	50 ppm, 8-h TWA

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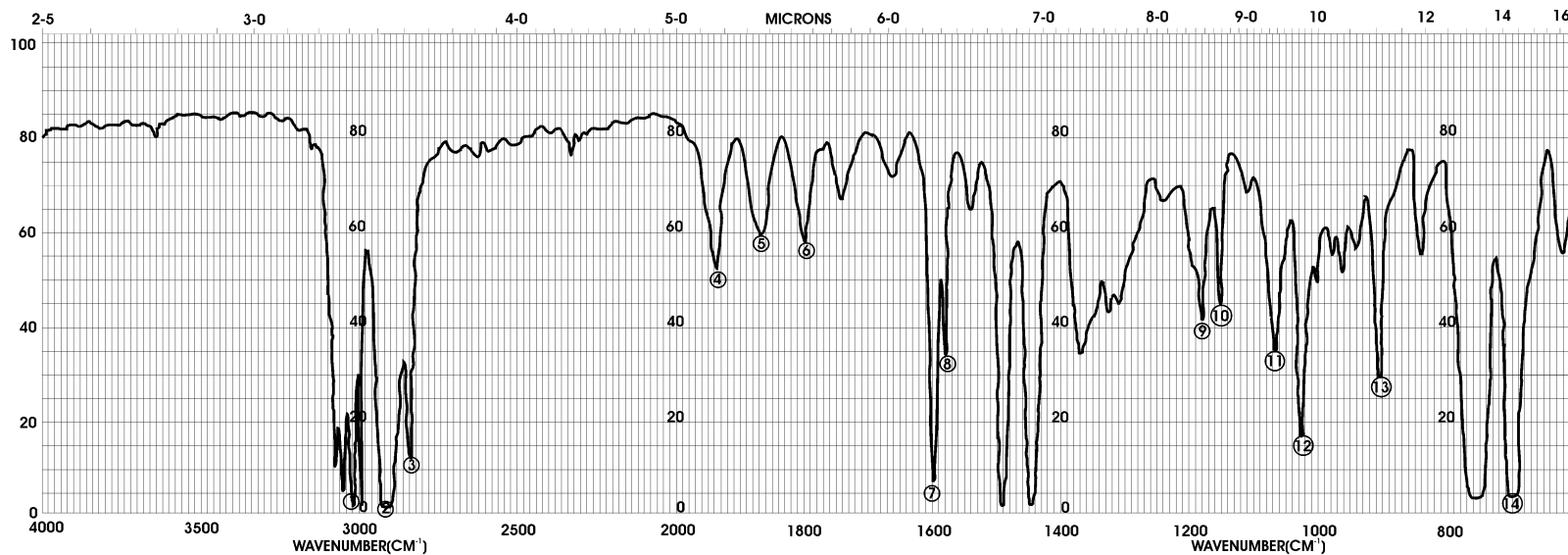
*Note:* Viscous, odorless, moderately combustible liquid used for mull preparation; relatively low toxicity; soluble in benzene, chloroform, carbon disulfide, ethers; incompatible with oxidizing materials and amines. Synonyms: mineral oil, adepsine oil, lignite oil.

## POLYSTYRENE WAVENUMBER CALIBRATION

The following are wavenumber readings assigned to the peaks on the spectrum:

1	—	3027.1	6	—	1801.6	11	—	1069.1
2	—	2924.0	7	—	1601.4	12	—	1028.0
3	—	2850.7	8	—	1583.1	13	—	906.7
4	—	1944.0	9	—	1181.4	14	—	698.9
5	—	1871.0	10	—	1154.3			

*Note:* Film thickness = 50  $\mu\text{m}$ .



POLYSTYRENE

## INFRARED ABSORPTION CORRELATION CHARTS

The following pages provide infrared absorption correlation charts. These charts are based upon the work of Professor Emeritus Charles F. Hammer of Georgetown University and are reproduced with permission.

Key:

AR = Aromatic

b = Broad

sd = Solid

sn = Solution

sp = Sharp

? = Unreliable

Strong



Medium

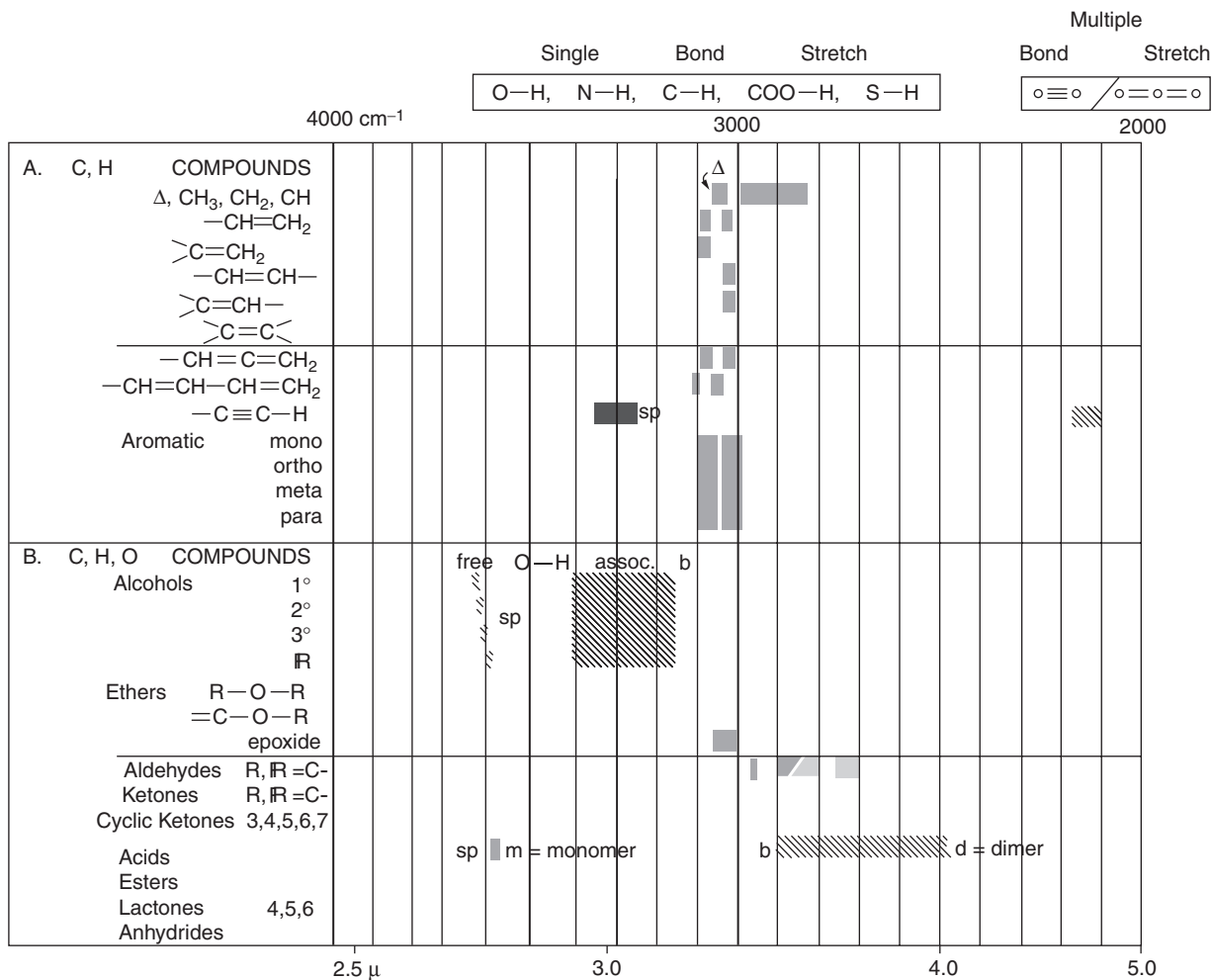


Weak



Variable

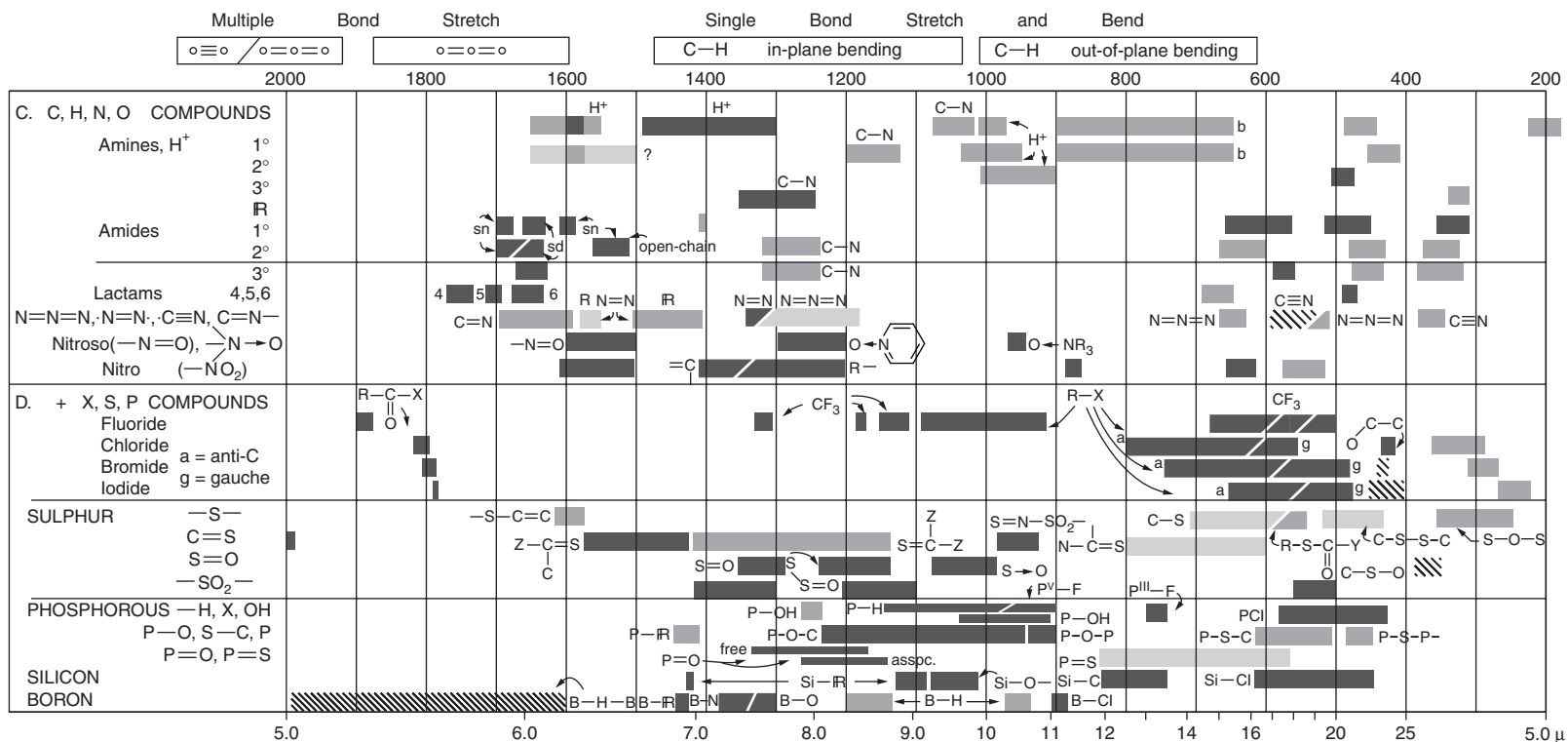




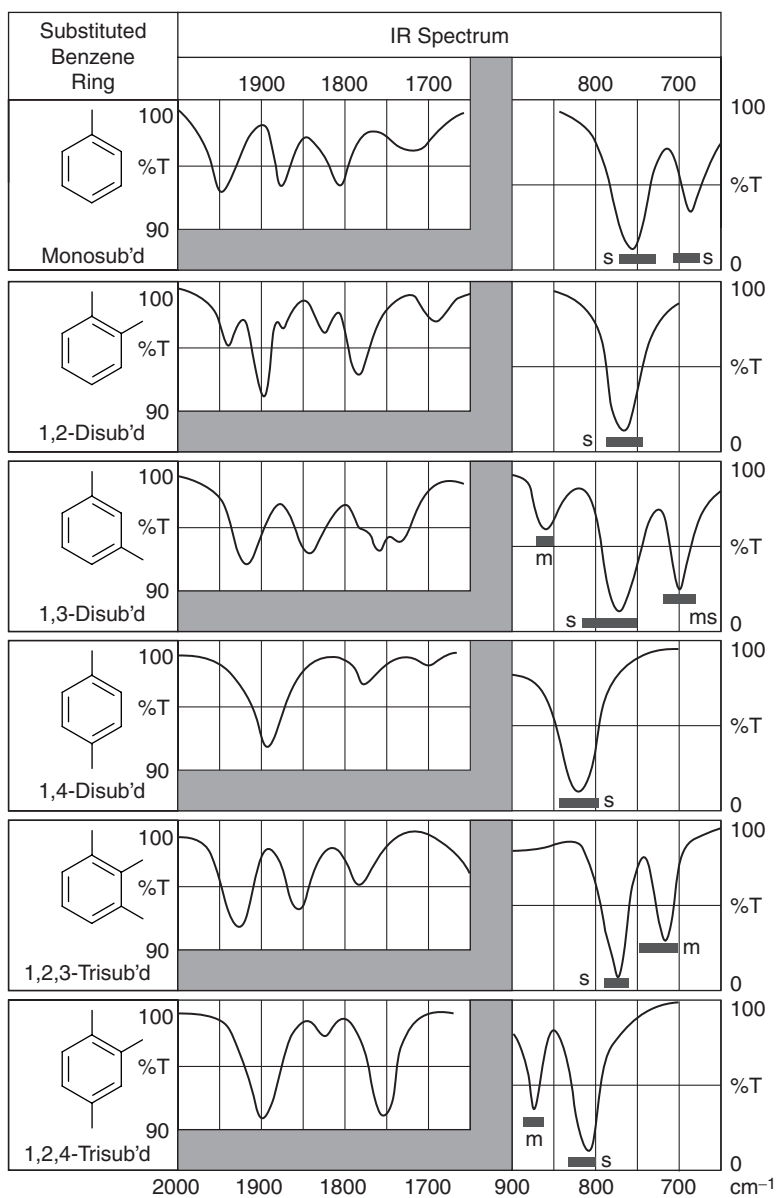




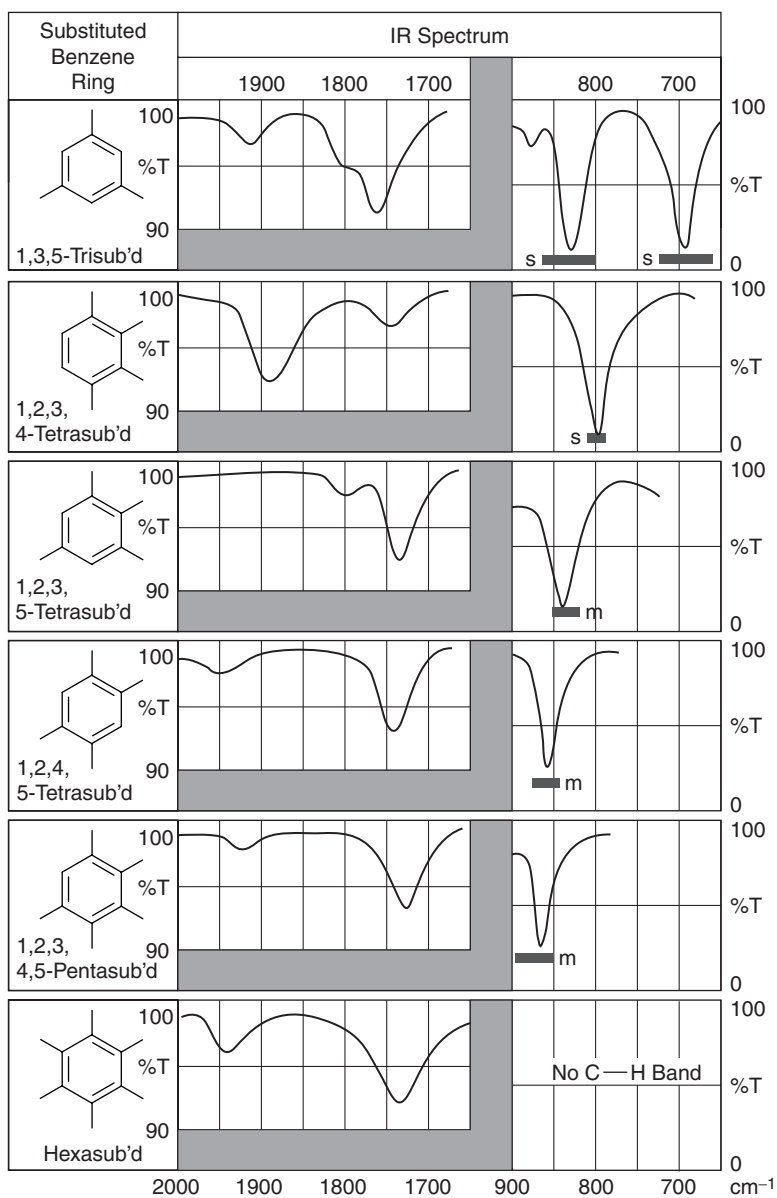




# AROMATIC SUBSTITUTION BANDS



# AROMATIC SUBSTITUTION BANDS



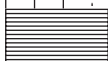

## Carbonyl Infrared Absorptions

Carbonyl	Wavenumber, $\text{cm}^{-1}$						
	1850	1800	1750	1700	1650	1600	1550
Aliphatic anhydrides of carboxylic acids		1825	1754				
Aromatic anhydrides of carboxylic acids		1802	1754				
Chlorides of carboxylic acids		1812					
Carboxylic acids (monomers)			1776				
Phenyl esters			1770				
Vinyl esters of carboxylic acids			1770				
Vinylidene esters of carboxylic acids			1764				
	5.41	5.56	5.71	5.88	6.06	6.25	6.45
	Wavelength, $\mu\text{m}$						

## Carbonyl Infrared Absorptions

Carbonyl	Wavenumber, $\text{cm}^{-1}$						
	1850	1800	1750	1700	1650	1600	1550
Vinyl-type carbonates			1761				
Normal carbonates			1751				
Methyl esters of carboxylic acids			1748				
Esters of carboxylic acids			1736				
Esters of formic acid			1733				
Aldehydes			1736				
Aliphatic ketones			1724				
	5.41	5.56	5.71	5.88	6.06	6.25	6.45
	Wavelength, $\mu\text{m}$						

## Carbonyl Infrared Absorptions

Carbonyl	Wavenumber, $\text{cm}^{-1}$						
	1850	1800	1750	1700	1650	1600	1550
Aromatic ketones						1680–1645	
Carboxylic acids (dimers)					1720–1700		
Carbamates					1689		
Amides (1°) of carboxylic acids					1684		
Amides (2°) of carboxylic acids					1669		
Amides (3°) of carboxylic acids					1667		
Salts of carboxylic acids							1575
	5.41	5.56	5.71	5.88	6.06	6.25	6.45
	Wavelength, $\mu\text{m}$						



## MID-RANGE INFRARED ABSORPTIONS OF MAJOR CHEMICAL FAMILIES

The following tables provide expected IR absorptions of the major chemical families.<sup>1-23</sup> The ordering of these tables is hydrocarbons, oxygen compounds, nitrogen compounds, sulfur compounds, silicon compounds, phosphorus compounds, and halogen compounds.

### Abbreviations

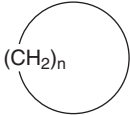
s	=	Strong	1°	=	primary
m	=	Medium	2°	=	secondary
w	=	Weak	3°	=	tertiary
vs	=	Very strong			
vw	=	Very weak			
sym	=	Symmetrical			
asym	=	Asymmetrical			

## REFERENCES

1. Nakanishi, K. and Solomon, P.H., *Infrared Absorption Spectroscopy*, Holden-Day, Inc., San Francisco, 1977.
2. Conley, R.T., *Infrared Spectroscopy*, 2nd ed., Allyn and Bacon, Boston, 1972.
3. Silverstein, R.M. and Webster, F.X., *Spectrometric Identification of Organic Compounds*, John Wiley & Sons, New York, 1997.
4. Williams, D.H. and Fleming, I., *Spectroscopic Methods in Organic Chemistry*, McGraw-Hill, London, 1973.
5. Lambert, J.B., Shuzvell, H.F., Verbit, L., Cooks, R.G., and Stout, G.H., *Organic Structural Analysis*, MacMillan Pub. Co., New York, 1976.
6. Meyers, C.Y., *Eighth Annual Report on Research, 1963, Sponsored by the Petroleum Research Fund*, American Chemical Society, Washington, D.C., 1964.
7. Kucsman, A., Ruff, F., and Kapovits, I., Bond system of N-acylsulfilimines. I. Infrared spectroscopic investigation of N-sulfonylsulfilimines, *Tetrahedron*, 25, 1575, 1966.
8. Kucsman, A., Kapovits, I., and Ruff, F., Infrared absorption of N-acylsulfilimines, *Acta Chim. Acad. Sci. Hung.*, 40, 75, 1964.
9. Kucsman, A., Ruff, F., and Kapovits, I., Bond system of N-acylsulfilimines. V. IR spectroscopic study on N-(p-nitrophenylsulfonyl) sulfilimines, *Acta Chim. Acad. Sci. Hung.*, 54, 153, 1967.
10. Shah, J.J., Iminosulfuranes (sulfilimines): infrared and ultraviolet spectroscopic studies, *Can. J. Chem.*, 53, 2381, 1975.
11. Tsujihara, K., Furukawa, N., and Oae, S., Sulfilimine. II. IR, UV and NMR spectroscopic studies, *Bull. Chem. Soc. Jpn.*, 43, 2153, 1970.
12. Fuson, N., Josien, M.L., and Shelton, E.M., An infrared spectroscopic study of the carbonyl stretching frequency in some groups of ketones and quinones, *J. Am. Chem. Soc.*, 76, 2526, 1954.
13. Davis, F.A., Friedman, A.J., and Kluger, E.W., Chemistry of the sulfur-nitrogen bond. VIII. N-alkylidenesulfinamides, *J. Am. Chem. Soc.*, 96, 5000, 1974.
14. Krueger, P.J. and Fulea, A.O., Rotation about the C-N bond in thioamides: influence of substituents on the potential function, *Tetrahedron*, 31, 1813, 1975.
15. Baumgarten, H.E. and Petersen, J.M., Reactions of amines. V. Synthesis of  $\alpha$ -aminoketones, *J. Am. Chem. Soc.*, 82, 459, 1960.
16. Gaset, A., Lafaille, L., Verdier, A., and Lattes, A., Infrared spectra of  $\alpha$ -aminoketones: configurational study and evidence of an enol form, *Bull. Soc. Chim. Fr.*, 10, 4108, 1968.
17. Cagniant, D., Faller, P., and Cagniant, P., Contribution in the study of condensed sulfur heterocycles. XVII. Ultraviolet and infrared spectra of some alkyl derivatives of thianaphthene, *Bull. Soc. Chim. Fr.*, 2410, 1961.

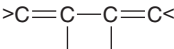
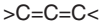

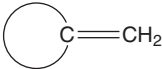
18. Tamres, M. and Searles, S., Jr., Hydrogen bonding abilities of cyclic sulfoxides and cyclic ketones, *J. Am. Chem. Soc.*, 81, 2100, 1959.
19. George, W.O., Goodman, R.C.W., and Green, J.H.S., The infra-red spectra of alkyl mercapturic acids, their sulphoxides and sulphones, *Spectrochim. Acta*, 22, 1741, 1966.
20. Cairns, T., Eglinton, G., and Gibson, D.T., Infra-red studies with sulphoxides. Part I. The S=O stretching absorptions of some simple sulphoxides, *Spectrochim. Acta*, 20, 31, 1964.
21. Hadzi, D., Hydrogen bonding in some adducts of oxygen bases with acids. Part I. Infrared spectra and structure of crystalline adducts of some phosphine, arsine, and amine oxides, and sulphoxides with strong acids, *J. Chem. Soc.*, 5128, 1962.
22. Currier, W.F. and Weber, J.H., Complexes of sulfoxides. I. Octahedral complexes of manganese (II), iron (II), cobalt (II), nickel (II), and zinc (II), *Inorg. Chem.*, 6, 1539, 1967.
23. Kucsman, A., Ruff, F., and Tanacs, B., IR spectroscopic study of N<sup>15</sup> labeled acylsulfilimines, *Int. J. Sulfur Chem.*, 8, 505, 1976.

## Hydrocarbon Compounds

Family	General Formula	Wavenumbers (cm <sup>-1</sup> )			
		C–H Stretch	C–H Bend	C–C Stretch	C–C Bend
Alkanes Acyclic	$C_nH_{2n+2}$				
Straight chain	$CH_3(CH_2)_nCH_3$	3000–2840 (s/m) CH <sub>3</sub> – (asym): 3000–2960 (s) CH <sub>3</sub> – (sym): 2880–2870 (s) >CH <sub>2</sub> (asym): 2930–2920 (s) >CH <sub>2</sub> (sym): 2860–2840 (s)	Below 1500 (w/m/s) CH <sub>3</sub> – (asym): 1460–1440 (s) CH <sub>3</sub> – (sym): 1380–1370 (s) >CH <sub>2</sub> (scissoring): ~1465 (s) >CH <sub>2</sub> (rocking): ~720 (s) >CH <sub>2</sub> (twisting and wagging): 1350–1150 (w)	1200–800 (w) (not of practical value for definitive assignment)	Below 500 (not of practical value for definitive assignment)
Branched	$\begin{array}{c} R^1-CH-R^3 \\   \\ R^2 \end{array}$	C–H (3°): ~2890 (vw)	gem Dimethyl [(CH <sub>3</sub> ) <sub>2</sub> CH–]: 1380, 1370 (m, symmetrical doublet) <i>tert</i> -Butyl [(CH <sub>3</sub> ) <sub>3</sub> C–]: 1390, 1370 (m, asymmetrical doublet; latter more intense) CH <sub>3</sub> – rocking: 930–920 (w, not reliable)		
Cyclic		Same as in acyclic alkanes; ring strain increases the wavenumbers up to 3100 cm <sup>-1</sup>	>CH <sub>2</sub> (scissoring): lower than in acyclic alkanes (10–15 cm <sup>-1</sup> )		

# Hydrocarbon Compounds (continued)

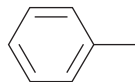
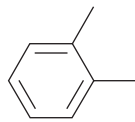
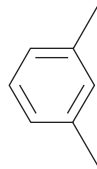

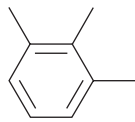
Family	General Formula	Wavenumbers (cm <sup>-1</sup> )				Notes
		>C=C< Stretch	>C=C-H Stretch	>C=C-H Bend (In-Plane)	>C=C-H Bend (Out-of-Plane)	
Alkenes (olefins)	C <sub>n</sub> H <sub>2n</sub>	1670–1600	Above 3000			
Acyclic						
Nonconjugated		1667–1640 (m)				
Monosubstituted (vinyl)	R <sup>1</sup> CH=CH <sub>2</sub>	1658–1648 (m)	3082–3000 (m)	1420–1415 (m) (scissoring)	~995 (m) ~919 (m)	
Disubstituted						
<i>cis</i> -	$\begin{array}{cc} \text{R}^1 & \text{R}^2 \\ >\text{C}=\text{C}< \\ \text{H} & \text{H} \end{array}$	1662–1652 (m)	3030–3015 (m)	~1406 (m)	715–675 (s) (rocking)	C–H rocking not dependable for definitive assignment
<i>trans</i> -	$\begin{array}{cc} \text{R}^1 & \text{H} \\ >\text{C}=\text{C}< \\ \text{H} & \text{R}^2 \end{array}$	1678–1668 (w)	3030–3020 (m)	1325–1275 (m) (deformation)	~965 (s) (rocking)	>C=C< stretch may not be detected due to symmetry
Vinylidene	$\begin{array}{cc} \text{R}^1 & \text{H} \\ >\text{C}=\text{C}< \\ \text{R}^2 & \text{H} \end{array}$	1658–1648 (m)	3090–3080 (m) ~2980 (m)	~1415 (m)	~890 (s) (rocking)	
Trisubstituted	$\begin{array}{cc} \text{R}^1 & \text{H} \\ >\text{C}=\text{C}< \\ \text{R}^2 & \text{R}^3 \end{array}$	1675–1665 (w)	3090–3080 (w)	~1415 (w)	840–800 (m) (deformation)	
Tetrasubstituted	$\begin{array}{cc} \text{R}^1 & \text{R}^3 \\ >\text{C}=\text{C}< \\ \text{R}^2 & \text{R}^4 \end{array}$	~1670 (vw)	—	—	—	>C=C< stretch may not be detected due to symmetry

Conjugated		1610–1600 (m) (frequently a doublet)	3050 (vw)		~980 (rocking)	Conjugation of an olefinic >C=C< with an aromatic ring raises the frequency by 20–25 cm <sup>-1</sup>
Cumulated		2000–1900 (m)	3300 (m)	2000–1900 (s) 1800–1700 (w)	880–850 (s)	
Cyclic		1640–1560 (variable)			697–625 (w) (wagging)	>C=C< stretch is coupled with C–C stretch of adjacent bonds; alkyl substitution increases the >C=C< absorption frequency
External exocyclic		1781–1650	3080, 2995 (m)	~1300 (w)		>C=C< frequency increases with decreasing ring size

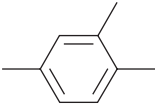
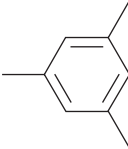
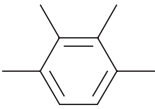
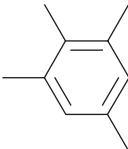
### Hydrocarbon Compounds (continued)

Family	General Formula	Wavenumbers (cm <sup>-1</sup> )			Notes
		—C≡C— Stretch	—C≡C—H Stretch	C—H Bend	
Alkynes Nonconjugated	C <sub>n</sub> H <sub>2n-2</sub>				
Terminal	R <sup>1</sup> —C≡C—H	2150–2100 (m)	3310–3200 (m) (sharp)	700–610 (s) 1370–1220 (w) (overtone)	—C≡C—H stretch peak is narrower than that of —OH or —NH stretch, which are broader due to hydrogen bonding
Nonterminal	R <sup>1</sup> —C≡C—R <sup>2</sup>	2260–2190 (vw)	—	700–610 (s) 1370–1220 (w) (overtone)	
Conjugated Terminal	R <sup>1</sup> —C≡C—C≡C—H	2200, 2040 (doublet)	3310–3200 (m) (sharp)	700–610 (s) 1370–1220 (w) (overtone)	
Nonterminal	R <sup>1</sup> —C≡C—C≡C—R <sup>2</sup>	2200, 2040 (doublet)	—	700–610 (s) 1370–1220 (w) (overtone)	

# Hydrocarbon Compounds (continued)

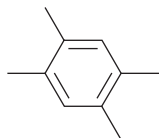
Family	General Formula	Wavenumbers (cm <sup>-1</sup> )			Notes
		H>C=C< Stretch	>C=C< Stretch	>C-H Bend (Out-of-Plane)	
Aromatic compounds					All show weak combination and overtone bands between 2000 and 16,500 cm <sup>-1</sup> ; see aromatic substitution pattern chart
Monosubstituted		3100–3000	1600–1500	770–730 (s) 710–690 (s)	
Disubstituted 1,2-		3100–3000	1600–1500	770–735 (s)	
1,3-		3100–3000	1600–1500	810–750 (s) 710–690 (s)	
1,4-		3100–3000	1600–1500	833–810 (s)	
Trisubstituted 1,2,3-		3100–3000	1600–1500	780–760 (s) 745–705 (m)	

# Hydrocarbon Compounds (continued)

Family	General Formula	Wavenumbers (cm <sup>-1</sup> )			Notes
		H>C=C< Stretch	>C=C< Stretch	>C-H Bend (Out-of-Plane)	
1,2,4-		3100–3000	1600–1500	885–860 (m) 825–805 (s)	
1,3,5-		3100–3000	1600–1500	865–810 (s) 730–765 (m)	
Tetrasubstituted 1,2,3,4-		3100–3000	1600–1500	810–800	
1,2,3,5-		3100–3000	1600–1500	850–840	



1,2,4,5-



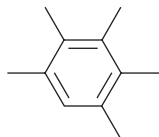
3100–3000

1600–1500

870–855

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Pentasubstituted



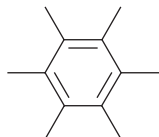
3100–3000

1600–1500

~870

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Hexasubstituted



3100–3000

1600–1500

Below 500

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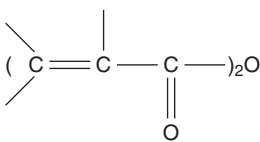
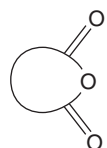
# Organic Oxygen Compounds

Family	General Formula	Wavenumbers (cm <sup>-1</sup> )			Notes
		O–H Stretch	>C–O Stretch	–O–H Bend	
Acetals	$\begin{array}{c} \text{OR}^2 \\   \\ \text{R}^1-\text{C}-\text{H} \\   \\ \text{OR}^3 \end{array}$		1195–1060 (s) (three bands) 1055–1040 (s) (sometimes obscured)		
Acyl halides	R–C(=O)X X = halogen				See Organic Halogen Compounds
Alcohols	R–OH	3650–3584 (s, sharp) for very dilute solutions or vapor phase spectra 3550–3200 (s, broad) for less dilute solutions where intermolecular hydrogen bonding is likely to occur Intramolecular hydrogen bonding is responsible for a broad, shallow peak in the range of 3100–3050 cm <sup>-1</sup>		1420–1300(s)	$\alpha$ -Unsaturation decrease >C–O stretch by 30 cm <sup>-1</sup> ; liquid spectra of alcohols show a broad out-of-plane bending band (769–650, s)
Primary	R–CH <sub>2</sub> OH		~1050	~1420 (m) and ~1330 (m) (coupling of O–H in-plane bending and C–H wagging)	
Secondary	$\begin{array}{c} \text{R}^1-\text{CHOH} \\   \\ \text{R}^2 \end{array}$		~1100	~1420 (m) and ~1330 (m) (coupling of O–H in-plane bending and C–H wagging)	
Tertiary	$\begin{array}{c} \text{R}^2 \\   \\ \text{R}^1-\text{C}-\text{OH} \\   \\ \text{R}^3 \end{array}$		~1150	Only one band (1420–1330 cm <sup>-1</sup> ), position depending on the degree of hydrogen bonding	

Organic Oxygen Compounds (continued)

Family	General Formula	Wavenumbers (cm <sup>-1</sup> )		Notes
		>C=O Stretch	-C(=O)H Stretch	
Aldehydes	R-CHO		~2820 (m), ~2720 (m) Fermi resonance between C-H stretch and first overtone of the aldehydic C-H bending	
Saturated, aliphatic	R = alkyl	1720–1720 (s)		
Aryl	R = aryl	1705–1695 (s)	~2900 (m), ~2750 (m) (aromatic)	
$\alpha,\beta$ -Unsaturated	>C=C-CHO	1700–1680 (s)		
$\alpha,\beta,\gamma,\delta$ -Unsaturated	>C=C-C=C-CHO	1680–1660 (s)		
$\beta$ -Ketoaldehyde	-C(=O)C-CHO	1670–1645 (s) (lowering is possible due to intramolecular hydrogen bonding in enol form)		
$\alpha$ -Halo-	$\begin{array}{c} >\text{C}-\text{CHO} \\   \\ \text{X} \end{array}$ X=halogen	~1740 (s)		

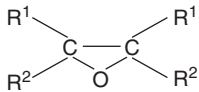
Organic Oxygen Compounds (continued)

Family	General Formula	Wavenumbers (cm <sup>-1</sup> )		Notes
		>C=O Stretch	>C–O Stretch	
Amides				See Organic Nitrogen Compounds
Anhydrides	>C(=O)O(=O)C<			
Saturated acyclic	>C(=O)O(=O)C<	~1820 (s) (asym) ~1760 (m/s) (sym)	1300–1050 (s) (one or two bands)	
Conjugated acyclic	 <p>(or Ar-CO)<sub>2</sub>O</p>	1795–1775 (s) (asym) 1735–1715 (m/s) (sym)	1300–1050 (s) (one or two bands)	
Cyclic		Ring strain raises band to higher frequencies (up to 1850 and 1790 cm <sup>-1</sup> ); conjugation does not reduce the frequency considerably	1300–1175 (s) 950–910 (s)	

Organic Oxygen Compounds (continued)

Family	General Formula	Wavenumbers (cm <sup>-1</sup> )				Notes
		>C=O Stretch	>C–O Stretch	–O–H Stretch	–O–H Bend	
Carboxylic acids						
Monomer, saturated	R–COOH	~1760 (s)	~1420	3550 (s)	~1250 (m/s)	
Monomer, aromatic	Ar–COOH	1730–1710	~1400	3500 (s)	~1250 (m/s)	
Dimer, saturated	<p>R = alkyl</p>	1720–1706 (s)	1315–1280 (m) (sometimes doublet)	3300–2500 (s, broad)	900–860 (m, broad) (out-of-plane)	700–610 (s) 1370–1220 (w) (overtone)
Dimer, α,β-unsaturated (or aromatic)	<p>R = alkenyl</p>	1700–1680 (s)	1315–1280 (m) (sometimes doublet)	3300–2500 (s, broad)	900–860 (m, broad) (out-of-plane)	

Organic Oxygen Compounds (continued)

Family	General Formula	Wavenumbers (cm <sup>-1</sup> )		Notes
		>C=O Stretch	>C–O Stretch	
Salt	R–COO <sup>-</sup>	1610–1550 (s) asym CO <sub>2</sub> <sup>-</sup> ~1400 (s) sym CO <sub>2</sub> <sup>-</sup>		
Cyanates	R–C≡N→O			See Organic Nitrogen Compounds
Epoxides				~1250 (s) (ring breathing, sym) 950–810 (s) (asym) 840–810 (s) (C–H bend) 3050–2990 (m/s) (C–H stretch)
Esters	R <sup>1</sup> –COOR <sup>2</sup>			
Saturated, aliphatic	R <sup>1</sup> , R <sup>2</sup> = alkyl	1750–1735 (s) α-Halogen substitution results in an increase in wavenumbers (up to 30 cm <sup>-1</sup> )	1210–1163 (s) [acetates only: 1240 (s)]	(O–C–C) 1046–1031 (s) (1° alcohol) ~1100 (s) (2° alcohol)
Formates	R <sup>1</sup> = H, R <sup>2</sup> = alkyl	1730–1715 (s)	~1180 (s), ~1160 (s)	

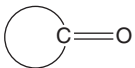
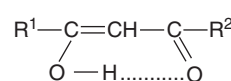
$\alpha,\beta$ -Unsaturated	$>\text{C}=\text{C}-\text{COOR}^2$ $\text{R}^2 = \text{alkyl}$	1730–1715 (s)	1300–1250 (s) 1200–1050 (s)
Benzoate	$\text{C}_6\text{H}_5-\text{COOR}^2$ $\text{R}^2 = \text{alkyl}$	1730–1715 (s)	1310–1250 (s) 1180–1100 (s)
Vinyl	$\text{R}^1-\text{COOCH}=\text{CH}_2$ $\text{R}^1 = \text{alkyl}$	1775–1755 (s)	1300–1250 (s) ~1210 (vs)
Phenyl	$\text{R}^1-\text{COOC}_6\text{H}_5$ $\text{R}^1 = \text{alkyl}$	~1770 (s)	1300–1200 (s) 1190–1140 (s)
$\alpha$ -Ketoesters	$-\text{C}(=\text{O})\text{COOR}^2$ $\text{R}^2 = \text{alkyl}$	1775–1740 (s)	1300–1050 (s) (two peaks)
$\beta$ -Ketoesters	$-\text{C}(=\text{O})-\text{C}-\text{C}(=\text{O})\text{R}^2$ $\text{R}^2 = \text{alkyl}$	~1735 (s) ~1650 (s) (due to enolization) $-\text{C}=\text{C}-\text{C}-\text{OR}^2$             O-H ...O	1300–1050 (s) (two peaks)
Aryl benzoates	$\text{R}^1-\text{COOR}^2$ $\text{R}^1, \text{R}^2 = \text{aryl}$	~1735 (s)	1300–1050 (s) (two peaks)

**Organic Oxygen Compounds (continued)**


Family	General Formula	Wavenumbers (cm <sup>-1</sup> )		Notes
		>C–O–C< Stretch Asymmetrical	>C–O–C< Stretch Symmetrical	
Ethers	R <sup>1</sup> –O–R <sup>2</sup>	1150–1085 (s)	Very hard to trace	
Aliphatic	R <sup>1</sup> , R <sup>2</sup> = alkyl	(branching off on the carbons adjacent to oxygen creates splitting)		
Aryl alkyl	R <sup>1</sup> = alkyl R <sup>2</sup> = aryl	1275–1200 (s) (high due to resonance)	1075–1020 (s)	
Vinyl	R <sup>1</sup> = vinyl R <sup>2</sup> = aryl	1225–1200 (s) (high due to resonance)	1075–1020 (s)	1660–1610 (m) (>C=CC) ~1000 (m), 909 (m) (>C=C–H) (wagging)
Imides	(R–C=O) <sub>2</sub> NH			See Organic Nitrogen Compounds
Isocyanates	R–N=C=O			See Organic Nitrogen Compounds
Ketals	$  \begin{array}{c}  \text{OR}^3 \\    \\  \text{R}^1 - \text{C} - \text{R}^2 \\    \\  \text{OR}^4  \end{array}  $	1190–1160 (s) 1195–1125 (s) 1098–1063 (s) 1055–1035 (s)		
Ketenes	>C=C=O			~2150 (s) (>C=C=O)



Organic Oxygen Compounds (continued)

Family	General Formula	Wavenumbers (cm <sup>-1</sup> )		Notes
		>C=O Stretch	>C=C< Stretch	
Ketones	R <sup>1</sup> C(=O)R <sup>2</sup>			>C=O overtone ~3400 (w); solid samples or solutions decrease >C=O stretch (10–20 cm <sup>-1</sup> ) α-Halogenation increases >C=O stretch (0–25 cm <sup>-1</sup> ) >C–H stretch is very weak (3100–2900 cm <sup>-1</sup> )
Aliphatic, saturated	R <sup>1</sup> , R <sup>2</sup> = alkyl	1720–1710 (s)		
α,β-Unsaturated	>C=C–C(=O)R <sup>2</sup> R <sup>2</sup> = alkyl	~1690 (s) ( <i>s-cis</i> ) ~1675 (s) ( <i>s-trans</i> )	1650–1600 (m)	
α,β-α <sup>1</sup> ,β <sup>1</sup> -Unsaturated	(>C=C–) <sub>2</sub> C=O	~1665 (s)	~1640 (m)	
α,β,γ,δ-Unsaturated	>C=C–C=C–C(=O)R <sub>2</sub> R <sup>2</sup> = alkyl	~1665 (s)	~1640 (m)	
Aryl	R <sup>1</sup> = aryl R <sup>2</sup> = alkyl	~1690 (s)	~1600, 1500 (m/s) (aromatic)	
Diaryl	R <sup>1</sup> , R <sup>2</sup> = aryl	~1665 (s)	~1600, 1500 (m/s) (aromatic)	
Cyclic		Three-membered: 1850 (s) Four-membered: 1780 (s) Five-membered: 1745 (s) Six-membered: 1715 (s) Larger than six-membered: 1705 (s)		Shows a shallow broad –OH band (enol form) at 3000–2700 cm <sup>-1</sup>  
α-Keto ( <i>s-trans</i> )	R <sup>1</sup> –C(=O)COR <sup>2</sup>	~1720 (s) (aliphatic) ~1680 (s) (aromatic)		
β-Keto	R <sup>1</sup> COCH <sub>2</sub> COR <sup>2</sup>	~1720 (s) (two bands)	1640–1580 (m, broad) Due to enol form	
α-Amino ketone hydrochlorides	R <sup>1</sup> COCH <sub>2</sub> NH <sub>3</sub> <sup>+</sup> Cl <sup>–</sup>			
α-Amino ketones	R–COCH <sub>2</sub> NR <sub>2</sub>			>C=O decreases 10–15 cm <sup>-1</sup> with electron deactivating p-substituents  Strong bands at 3700–3600 cm <sup>-1</sup> (–OH) and 1700–1600 cm <sup>-1</sup> (>C=O) due to the presence of enolic forms

Organic Oxygen Compounds (continued)

Family	General Formula	Wavenumbers (cm <sup>-1</sup> )			Notes
		>C=O Stretch	>C=C< Stretch	>C–O stretch	
Lactams (cyclic amides)					See Organic Nitrogen Compounds
Lactones (cyclic esters)					
Saturated	x = 4	~1735 (s)		1300–1050 (s, two peaks)	
α-	x = 3	~1770 (s)		1300–1050 (s, two peaks)	
γ-	x = 2	~1840 (s)		1300–1050 (s, two peaks)	
β-					
Unsaturated, α- to the carbonyl (>C=O)	x = 4 x = 3	~1720 (s) ~1750 (s) (doublet 1785–1755 cm <sup>-1</sup> when α-hydrogen present)		1300–1050 (s, two peaks) 1300–1050 (s, two peaks)	
Unsaturated, α- to the oxygen	x = 4 x = 3	~1760 (s) ~1790 (s)	~1685 (s) ~1660 (s)	1300–1050 (s, two peaks) 1300–1050 (s, two peaks)	
Unsaturated, α- to the carbonyl and α- to the oxygen	x = 4 (α-pyrone, coumarin)	1775–1715 (s, doublet)	1650–1620 (s) 1570–1540 (s)	1300–1050 (s, two peaks)	
Nitramines	R <sup>1</sup> >N–NO <sub>2</sub> R <sub>2</sub>				See Organic Nitrogen Compounds
Nitrates	R–NO <sub>3</sub>				See Organic Nitrogen Compounds
Nitro compounds	R–NO <sub>2</sub>				See Organic Nitrogen Compounds
Nitrosamines	R <sub>1</sub> >N–N=O R <sub>2</sub>				See Organic Nitrogen Compounds
N-Nitroso compounds	R <sup>1</sup> –N–N=O   R <sup>2</sup>				See Organic Nitrogen Compounds

Organic Oxygen Compounds (continued)

Family	General Formula	Wavenumbers (cm <sup>-1</sup> )			Notes
		>C–O Stretch	–O–H Stretch	>C=O Stretch	
Peroxides	R <sup>1</sup> –O–O–R <sup>2</sup>	–C–C–O–		–C(=O)O	
Aliphatic	R <sup>1</sup> , R <sup>2</sup> = alkyl	890–820 (vw)			
Aromatic	R <sup>1</sup> , R <sup>2</sup> = aromatic	~1000 (vw)			
Acyl, aliphatic	R <sup>1</sup> , R <sup>2</sup> = acyl (aliphatic)	890–820 (vw)		1820–1810 (s) 1800–1780 (s)	
Acyl, aromatic	R <sup>1</sup> , R <sup>2</sup> = acyl (aromatic)	~1000 (vw)		1805–1780 (s) 1785–1755 (s)	
Peroxyacids	R <sup>1</sup> –C(=O)OOH	~1260 (s)	3300–3250 (s, not as broad as in R–COOH)	1745–1735 (s) (doublet)	~1400 (m) ~850 cm <sup>-1</sup> (m, –O–O– stretch)
Peroxyacids, anhydride	(R <sup>1</sup> –COO) <sub>2</sub>	(–COO–OOC–)			
Alkyl	R <sup>1</sup> = alkyl	1815 (s), 1790 (s)			
Aryl	R <sup>1</sup> = aryl	1790 (s), 1770 (s)			

Organic Oxygen Compounds (continued)

Family	General Formula	Wavenumbers (cm <sup>-1</sup> )			Notes
		>C=O Stretch	–O–H Stretch	–O–H Bend	
Phenols	Ar–OH Ar = aryl	~1230 (m)	~3610 (m, sharp) (in CHCl <sub>3</sub> or CCl <sub>4</sub> solution) ~3100 (m, broad) (in neat samples)	1410–1310 (m, broad) (in-plane) ~650 (m) (out-of-plane)	
Phosphates	(R <sup>1</sup> O) <sub>3</sub> P=O				See Organic Phosphorus Compounds
Phosphinates	(R <sup>1</sup> O)P(=O)H <sub>2</sub>				See Organic Phosphorus Compounds
Phosphine oxides	R <sub>3</sub> P=O				See Organic Phosphorus Compounds
Phosphonates	(R <sup>1</sup> O) <sub>2</sub> P(=O)H				See Organic Phosphorus Compounds
Phosphorus acids	R <sub>2</sub> P(=O)OH				See Organic Phosphorus Compounds
Pyrophosphates	(R–P=O) <sub>2</sub> O				See Organic Phosphorus Compounds

**Organic Oxygen Compounds (continued)**

Family	General Formula	Wavenumbers (cm <sup>-1</sup> )		Notes
		>C=O Stretch	>C=C< Stretch	
Quinones				
1,2-		~1675 (s)	~1600 (s)	
1,4-		~1675 (s)	~1600 (s)	
Silicon compounds				See Organic Silicon Compounds
Sulfates				See Organic Sulfur Compounds
Sulfonamides				See Organic Sulfur Compounds
Sulfonates				See Organic Sulfur Compounds
Sulfones				See Organic Sulfur Compounds
Sulfonyl chlorides				See Organic Sulfur Compounds
Sulfoxides				See Organic Sulfur Compounds

# Organic Nitrogen Compounds

Family	General Formula	Wavenumbers (cm <sup>-1</sup> )			Notes
		C–N	N–H	Others	
Amides					
Primary	R <sup>1</sup> –CONH <sub>2</sub>	1400 (s) (stretch)	3520 (m) (stretch) 3400 (m) (stretch) 1655–1620 (m) (bend) 860–666 (m, broad) (wagging)	>C=O (1650) (s, solid state) (1690) (s, solution)	Lowering of N–H stretch occurs in solid samples due to hydrogen bonding; higher values arise in dilute samples
Secondary	R <sup>1</sup> –CONHR <sup>2</sup>	1400 (s) (stretch)	3500–3400 (w) (stretch) 1570–1515 (w) (bend) 860–666 (m, broad) (wagging)	>C=O (1700–1670) (s, solution); (1680–1630) (s, solid state) Band due to interaction of N–H (bend) and (C–N) (stretch) (~1250) (m, broad)	Lowering of N–H stretch occurs in solid samples due to hydrogen bonding; higher values arise in dilute samples
Tertiary	R <sup>1</sup> –CONR <sup>2</sup> R <sup>3</sup>	1400 (s) (stretch)	—	>C=O (1680–1630) (s); higher values are obtained with electron attracting groups attached to the nitrogen	
Amines					
Primary	R <sup>1</sup> –NH <sub>2</sub>	1250–1020 (m) (for nonconjugated amines) 1342–1266 (s) (for aromatic amines)	3500 (w) (stretch) 3400 (w) (stretch) 1650–1580 (m) (scissoring) 909–666 (m) (wagging)		
Secondary	R <sup>1</sup> –NHR <sup>2</sup>	1250–1020 (m) (for nonconjugated amines) 1342–1266 (s) (for aromatic amines)	3350–3310 (w) (stretch) 1515 (vw) (scissoring) 909–666 (m) (wagging)		
Tertiary	R <sup>1</sup> –NR <sup>2</sup> R <sup>3</sup>	1250–1020 (m) (for nonconjugated amines) 1342–1266 (s) (for aromatic amines)	—		
Amine salts					
Primary	RNH <sub>3</sub> <sup>+</sup> X <sup>-</sup>		3000–2800 (s) 2800–2200 (m) (series of peaks) 1600–1575 (m) 1550–1504 (m)		

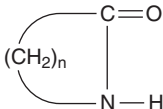
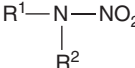
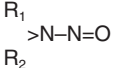
Secondary	$R_2NH_2^+X^-$	3000–2700 (s) 2700–2250 (m) (series of peaks) 2000 (w) 1620–1560 (m)	
Tertiary	$R_3NH^+X^-$	2700–2250 (s)	
Quaternary	$R_4N^+X^-$	—	
Amino acids (alpha)	$  \begin{array}{c}  R^1-CH-COO^- \\    \\  NH_2  \end{array}  $ $  \begin{array}{c}  R^1-CH-COO^- \\    \\  +NH_3  \end{array}  $ $  \begin{array}{c}  R^1-CH-COOH \\    \\  +NH_3  \end{array}  $	3100–2600 (s, broad) 2222–2000 (s, broad, overtone) 1610 (w) (bend) 1550–1485 (s) (bend)	–COO <sup>−</sup> (1600–1590) (s) –COOH (1755–1730) (s)
Ammonium ion	$NH_4^+$	3300–3040 (s) 2000–1709 (m) 1429 (s)	
Azides	$R-N_3$		2140 (s) (asym stretch, $N_3$ ) 1295 (s) (sym stretch, $N_3$ )
Azocompounds	$R^1-N=N-R^2$ ( <i>trans</i> )	Forbidden in IR but allowed in Raman spectrum (1576) (w); peak is lowered to 1429 $cm^{-1}$ in unsymmetrical p-electron-donating substituted azobenzenes	
Azoxy compounds	$R-N=N \rightarrow O$		1310–1250 (s)

Organic Nitrogen Compounds (continued)

Family	General Formula	Wavenumbers (cm <sup>-1</sup> )		Notes
		C–N Multiple Bond	Cumulated (–X=C=Y) Double Bond	
Cyano compounds (nitriles)	R–C≡N	2260–2240 (w) (aliphatic) 2240–2220 (m) (aromatic, conjugated)		Electronegative elements α- to the C≡N group reduce the intensity of the absorption
Diazonium salts	R–N≡N <sup>+</sup>			2280–2240 (m) (–N N) <sup>+</sup>
Imides	$\begin{array}{c} \text{R} - \text{C} - \text{NH} - \text{C} - \text{R} \\ \parallel \qquad \qquad \parallel \\ \text{O} \qquad \qquad \text{O} \end{array}$			1710, 1700 (>C=O six-membered ring) 1770, 1700 (>C=O five-membered ring)
Isocyanates	R–N=C=O		2273–2000 (s) (broad) (asym) 1400–1350 (w) (sym)	
Isocyanides (isonitriles)	R–N≡C	2400–2300 (w) (aliphatic) 2300–2200 (w) (aromatic)		
Isonitriles				See Isocyanides
Isothiocyanates	R–N=C=S		2140–2000 (s) (stretch)	
Ketene	$\begin{array}{c} \text{R}_1 \\ >\text{C}=\text{C}=\text{O} \\ \text{R}_2 \end{array}$		2150 (stretch); 1120	
Ketenimine	$\begin{array}{c} \text{R}_1 \\ >\text{C}=\text{C}=\text{N}- \\ \text{R}_2 \end{array}$		2000 (stretch)	



Organic Nitrogen Compounds (continued)

Family	General Formula	Wavenumbers (cm <sup>-1</sup> )			Others	Notes
		>C–N	>N–O (Asymmetric)	>N–O (Symmetric)		
Lactams					>C=O (s) (stretch) 1670 (six-membered ring) 1700 (five-membered ring) 1745 (four-membered ring) N–H (out-of-plane wagging) (800–700) (broad)	Add ~15 cm <sup>-1</sup> to every wavenumber in case of a >C=C< in conjugation; amide group is forced into the <i>cis</i> -conformation in rings of medium size
Nitramines			1620–1580 (s) (asym) 1320–1290 (s) (sym)			
Nitrates	RO–NO <sub>2</sub>				–N=O 1660–1625 (s) (asym) 1300–1225 (s) (asym) >N–O 870–833 (s) (stretch) 763–690 (s) (bend)	
Nitriles (cyano compounds)	R–C≡N					See Cyano compounds
Nitrites	RO–N=O				–N=O stretch 1680–1650 (vs) ( <i>trans</i> ) 1625–1610 (vs) ( <i>cis</i> ) >N–O stretch 850–750 (vs)	
Nitro compounds Aliphatic	R–NO <sub>2</sub> R–alkyl	870	1615–1540 (vs) (asym) 1390–1320 (vs) (sym)	1390–1320 (vs)	~610 (m) (CNO bend)	Aromatics absorb at lower frequencies than aliphatic
Aromatic	R=aryl	(Difficult to assign)	1548–1508 (s) (asym) 1356–1340 (s) (sym)	1356–1340 (s)		
Nitrosamines					>N–O stretch (1520–1500) (s) (vapor) (1500–1480) (s) (neat) N–N (1150–925) (m)	

Organic Nitrogen Compounds (continued)

Family	General Formula	Wavenumbers (cm <sup>-1</sup> )			Notes
		>C–N	>N–O (Asymmetric)	>N–O (Symmetric)	
N-Nitroso compounds	R–N=O			N=O stretch 1585–1539 (s) (3°, aliphatic) 1511–1495 (s) (3°, aromatic)	1 and 2°C — nitroso compounds are unstable and rearrange or dimerize
Pyridines	C <sub>5</sub> H <sub>5</sub> N			N–H (3075, 3030) (s) C–H (out-of-plane) (920–720) (s) (2000–1650) (overtone) C=C ring stretch (1600, 1570, 1500, 1435)	Characteristic substitution pattern: α-Substitution: (795–780), (755–745) β-Substitution: (920–880), (840–770), 720
Sulfilimines	$  \begin{array}{c}  \text{R}^1 \diagdown \\  \text{S}=\text{N}-\text{R}^3 \\  \text{R}^2 \diagup  \end{array}  $				See Organic Sulfur Compounds
Sulfonamides	R–SO <sub>2</sub> NH <sub>2</sub>				See Organic Sulfur Compounds
Thiocyanates	R–SC≡N				See Organic Sulfur Compounds

# Organic Sulfur Compounds

Family	General Formula	Wavenumbers (cm <sup>-1</sup> )			Notes
		>S=O (Asymmetric)	>S=O (Symmetric)	>S=N–	
Disulfides	R <sup>1</sup> –S–S–R <sup>2</sup>				–S–S– (<500) (w)
Mercaptans	R–S–H				–S–H (2600–2500) (w) Only significant frequency around that region; lowering of 50–150 cm <sup>-1</sup> due to hydrogen bonding
Mercapturic acids	$  \begin{array}{c}  \text{R}^2(\text{O}=\text{CNH}) \\    \\  \text{RSCH}_2\text{CH} \\    \\  \text{HOOC}  \end{array}  $	1295–1280 (s) (for sulfones)	1135–1100 (s) (for sulfones)		1025, 970 (>S→O) (for sulfoxides) Reduction of all >S=O frequencies due to H– bonding with –NH
Sulfates	(RO) <sub>2</sub> S(=O) <sub>2</sub>	1415–1380 (s)	1200–1185 (s)		
Sulfides	R <sup>1</sup> –S–R <sup>2</sup>				R–S– (700–600) (w)
Sulfilimines	R <sub>2</sub> S=N–R <sup>1</sup>				
<i>N</i> -Acyl	R <sub>2</sub> S=N–COR <sup>1</sup>			800 (s)	>C=O (1625–1600) (s)
<i>N</i> -Alkyl	R <sub>2</sub> S=N–R <sup>1</sup>			987–935 (s)	
<i>N</i> -Sulfonyl	R <sub>2</sub> S=N–SO <sub>2</sub> R <sup>1</sup>	1280–1200 (s) 1095–1030 (s)	1160–1135 (s)	980–901 (s)	
Sulfinamides, <i>N</i> -alkylidene	RS(O)N=CR <sub>2</sub>				1520 (amide II band) 1080 (s, S→O)
Sulfonamides	R–SO <sub>2</sub> NH <sub>2</sub>	1370–1335 (s)	1170–1155 (s)		>N–H (1°) (3390–3330) (s) (3300–3247) (s) >N–H (2°) (3265) (s) Solid phase spectra lower wavenumbers by 10–20 cm <sup>-1</sup>
Sulfonates	R <sup>1</sup> –SO <sub>2</sub> –OR <sup>2</sup>	1372–1335 (s)	1195–1168 (s)		Electron-donating groups on the aryl group cause higher-frequency absorption
Sulfones	R <sup>1</sup> –SO <sub>2</sub> –R <sup>2</sup>	1350–1300 (s)	1160–1120 (s)		Hydrogen bonding reduces the frequency of absorption slightly
Sulfonic acids (anhydrous)	R–SO <sub>3</sub> H	1350–1342 (s)	1165–1150 (s)		–OH (3300–2500) (s, broad) Hydrated sulfonic acids show broad bands at 1230–1150 cm <sup>-1</sup>
Sulfonic acids, salts	R–SO <sub>3</sub> <sup>–</sup>	ca. 1175 (s)	ca. 1055 (s)		

Organic Sulfur Compounds (continued)

Family	General Formula	Wavenumbers (cm <sup>-1</sup> )			Notes
		>S=O (Asymmetric)	>S=O (Symmetric)	>S=N–	
Sulfonyl chlorides	R–SO <sub>2</sub> Cl	1410–1380 (s)	1204–1177 (s)		
Sulfoxides Cyclic	R <sub>2</sub> S→O (CH <sub>2</sub> ) <sub>x</sub> S→O				>S→O (1070–1030) (s) x = 3 1192 (CCl <sub>4</sub> ) 1073 (CHCl <sub>3</sub> ) x = 4 1035 (CCl <sub>4</sub> ) 1020 (CHCl <sub>3</sub> ) x = 5 1053 (CCl <sub>4</sub> ) 1031 (CHCl <sub>3</sub> ) Hydrogen bonding reduces the frequency absorption slightly; electronegative substituents increase the >S→O frequency; inorganic complexation reduces the >S→O (up to 50 cm <sup>-1</sup> )
Thiocarbonyls (not trimerized into cyclic sulfides)	R <sup>1</sup> –C–R <sup>2</sup> (H)    S				>C=S (1250–1020) (s)
Thiocyanates	R–S–C≡N				–C≡N (2175–2140) (s); higher values for aryl thiocyanates
Thiol esters	R <sup>1</sup> –C–SR <sup>2</sup>    O				>C=O (1690) (s) (S-alkyl thioester) (1710) (s) (S-aryl thioester)
Thiols	R–SH				See Mercaptans
Thiophenols	Ar–SH				–S–H (2600–2500) (w)

# Organic Silicon Compounds

Family	General Formula	Wavenumbers (cm <sup>-1</sup> )					
		>Si-H Stretch	>Si-H Bend	>C-Si< Stretch	>C-H Bend	>Si-O- Stretch	-OH Stretch
Silanes	R <sub>x</sub> SiH <sub>y</sub>						
Monoalkyl	R-SiH <sub>3</sub>	2130–2100 (s)	890–860 (s)	890–690 (s)	~1260 (s) (rocking)		
Dialkyl	R <sub>2</sub> SiH <sub>2</sub>	~2135 (s)	890–860 (s)	820–800 (s)	~1260 (s) (rocking)		
Trialkyl	R <sub>3</sub> SiH	2360–2150 (s)	890–860 (s)	~840 (s) ~755 (s)	~1260 (s) (rocking)		
Tetraalkyl	R <sub>4</sub> Si			890–690 (s)	~1260 (s) (rocking)		
Alkoxy	R <sub>x</sub> <sup>1</sup> Si(OR <sup>2</sup> ) <sub>y</sub>			890–690 (s)	~1260 (s) (rocking)	1090–1080 (s) (doublet)	
Siloxanes	>Si-O-Si<					1110–1000 (s)	
Disiloxanes						(Si-O-Si)	
Cyclic trimer						~1053 (s)	
Cyclic tetramer						~1020 (s) ~1082 (s)	
Hydroxysilanes	R <sub>x</sub> Si(OH) <sub>y</sub>						~3680 (s) (confirmed by band at 870–820 cm <sup>-1</sup> )

# Organic Phosphorus Compounds

Family	General Formula	Wavenumbers (cm <sup>-1</sup> )				Notes
		>P=O Stretch	>P-H Stretch	>P-O-C< Stretch	-OH Stretch	
Phosphates Alkyl Aryl	O=P(OR) <sub>3</sub>	1300–1100 (s) (doublet) 1285–1260 (s) (doublet) 1315–1290 (s) (doublet)		~1050 (s) (alkyl) 950–875 (s) (aryl)		→P=O stretch can shift up to 65 cm <sup>-1</sup> due to solvent effect
Phosphinates	H <sub>2</sub> P-OR    O	1220–1180 (s)	~2380 (m) ~2340 (m) (sharp)	~1050 (s) (alkyl) 950–875 (s) (aryl)		
Phosphine oxides Alkyl Aryl	(R)H-PR <sub>1</sub> R <sub>2</sub>    O	1185–1150 (s) 1145–1095 (s)	2340–2280 (m) 2340–2280 (m)			→P=O decreases with complexation
Phosphates	H-P(OR) <sub>2</sub>    O	1265–1230 (s)	2450–2420 (m)	~1050 (s) (alkyl) 950–875 (s) (aryl)		
Phosphorus acids	R <sup>1</sup> P(=O)OH   R <sup>2</sup>	1240–1180 (vs)			2700–2200 (s, broad) (assoc)	
Phosphorus amides	(RO) <sub>2</sub> PNR <sup>1</sup> R <sup>2</sup>    O	1275–1200 (s)				
Pyrophosphates	R <sub>2</sub> P-O-PR <sub>2</sub>          O    O	1310–1200 (s) (single band)				

# Organic Halogen Compounds

Family	General Formula	Wavenumbers (cm <sup>-1</sup> )			=C–X Stretch
		>C–X Stretch	>CX <sub>2</sub> Stretch	–CH <sub>3</sub> Stretch	
Fluorides	X = F	1120–1010	1350–1200 (asym) 1200–1080 (sym)	1350–1200 (asym) 1200–1080 (sym)	1230–1100
Chlorides	X = Cl	830–500 1510–1480 (overtone)	845–795 (asym) ~620 (sym)		
Bromides	X = Br	667–290			
Iodides	X = I	500–200			

## COMMON SPURIOUS INFRARED ABSORPTION BANDS

The following table provides some of the common potential sources of spurious infrared absorptions that might appear on a spectrum.

**Common Spurious Infrared Absorption Bands**

Approximate Wavenumber (in $\text{cm}^{-1}$ )	Wavelength ( $\mu\text{m}$ )	Compound or Group	Origin
3700	2.70	$\text{H}_2\text{O}$	Water in solvent (thick layers)
3650	2.74	$\text{H}_2\text{O}$	Water in some quartz windows
3450	2.9	$\text{H}_2\text{O}$	Hydrogen-bonded water, usually in KBr disks
2900	3.44	$-\text{CH}_3, >\text{CH}_2$	Paraffin oil, residual from previous mulls
2350	4.26	$\text{CO}_2$	Atmospheric absorption, or dissolved gas
2330	4.30	$\text{CO}_2$	from a dry ice bath
2300 and 2150	4.35 and 4.65	$\text{CS}_2$	Leaky cells, previous analysis of samples dissolved in carbon disulfide
1996	5.01	$\text{BO}_2^-$	Metaborate in the halide window
1400–2000	5–7	$\text{H}_2\text{O}$	Atmospheric absorption
1820	5.52	$\text{Cl}_2\text{CO}$	Phosgene, decomposition product in purified $\text{CHCl}_3$
1755	5.7	Phthalic anhydride	Decomposition product of phthalate esters or resins; paint off-gas product
1700–1760	5.7–5.9	$>\text{C}=\text{O}$	Bottle-cap liners leached by sample
1720	5.8	Phthalates	Phthalate polymer plastic tubing
1640	6.1	$\text{H}_2\text{O}$	Water of crystallization entrenched in sample
1520	6.6	$\text{CO}_2$	Leaky cells, previous analysis
1430	7.0	$\text{CO}_3^{2-}$	Contaminant in halide window
1360	7.38	$\text{NO}_3^-$	Contaminant in halide window
1270	7.9	$-\text{SiO}-$	Silicone oil or grease
1000–1110	9–10	$-\text{Si}-\text{O}-\text{Si}-$	Glass; silicones
980	10.2	$\text{SO}_4^{2-}$	From decomposition of sulfates in KBr pellets
935	10.7	$(\text{CH}_2\text{O})_x$	Deposit from gaseous formaldehyde
907	11.02	$-\text{C}-\text{Cl}$	Dissolved R-12 (Freon-12)
837	11.95	$\text{NO}_3^-$	Contaminant in halide window
823	12.15	$\text{KNO}_3$	From decomposition of nitrates in KBr pellets
794	12.6	$\text{CCl}_4$ vapor	Leaky cells, from $\text{CCl}_4$ used as a solvent
788	12.7	$\text{CCl}_4$ liquid	Incomplete drying of cell or contamination, from $\text{CCl}_4$ used as a solvent
720 and 730	13.7 and 13.9	Polyethylene	Various experimental sources
728	13.75	$-\text{Si}-\text{F}$	$\text{SiF}_4$ , found in NaCl windows
667	14.98	$\text{CO}_3^{2-}$	Atmospheric carbon dioxide
Any	Any	Fringes	If refractive index of windows is too high, or if the cell is partially empty, or the solid sample is not fully pulverized



# Nuclear Magnetic Resonance Spectroscopy

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## PROPERTIES OF IMPORTANT NMR NUCLEI

The following table lists the magnetic properties required most often for choosing the nuclei to be used in NMR experiments.<sup>1-14</sup> Refer to several excellent texts and the literature for guidelines in nucleus selection.

### REFERENCES

1. Silverstein, R.M., Bassler, G.C., and Morrill, T.C., *Spectrometric Identification of Organic Compounds*, 5th ed., John Wiley & Sons, New York, 1991.
2. Yoder, C.H. and Shaeffer, C.D., *Introduction to Multinuclear NMR*, Benjamin/Cummings, Menlo Park, CA, 1987.
3. Gordon, A.J. and Ford, R.A., *The Chemist's Companion*, Wiley Interscience, New York, 1971.
4. Silverstein, R.M. and Webster F.X., *Spectrometric Identification of Organic Compounds*, 6th ed., John Wiley & Sons, New York, 1998.
5. Becker, E.D., *High Resolution NMR, Theory and Chemical Applications*, 2nd ed., Academic Press, New York, 1980.
6. Gunther, H., *NMR Spectroscopy: Basic Principles, Concepts and Applications in Chemistry*, John Wiley & Sons, New York, 2003.
7. Rahman, A.-U., *Nuclear Magnetic Resonance*, Springer-Verlag, New York, 1986.
8. Harris, R.K., NMR and the periodic table, *Chem. Soc. Rev.*, 5, 1, 1976.
9. Kitamaru, R., *Nuclear Magnetic Resonance: Principles and Theory*, Elsevier Science, Amsterdam, 1990.
10. Lambert, J.B., Holland, L.N., and Mazzola, E.P., *Nuclear Magnetic Resonance Spectroscopy: Introduction to Principles, Applications and Experimental Methods*, Prentice Hall, Englewood Cliffs, NJ, 2003.
11. Bovey, F.A. and Mirau, P.A., *Nuclear Magnetic Resonance Spectroscopy*, 2nd ed., Academic Press, New York, 1988.
12. Harris, R.K. and Mann, B.E., *NMR and the Periodic Table*, Academic Press, London, 1978.
13. Hore, P.J. and Hore, P.J., *Nuclear Magnetic Resonance*, Oxford University Press, Oxford, 1995.
14. Nelson, J.H., *Nuclear Magnetic Resonance Spectroscopy*, 2nd ed., John Wiley & Sons, New York, 2003.

Properties of Important NMR Nuclei

Isotope	Natural Abundance	Spin Number I	NMR Frequency <sup>a</sup> at Indicated Field Strength in kG				
			10.000	14.092	21.139	23.487	51.567
<sup>1</sup> H <sup>1</sup>	99.985	1/2	42.5759	60.0000	90.0000	100.0000	220.0000
<sup>1</sup> H <sup>2</sup>	0.015	1	6.53566	9.21037	13.81555	15.35061	33.77134
<sup>1</sup> H <sup>3 b</sup>	—	1/2	45.4129	63.9980	95.9971	106.6634	234.6595
<sup>6</sup> C <sup>13</sup>	1.108	1/2	10.7054	15.0866	22.6298	25.1443	55.3174
<sup>7</sup> N <sup>14</sup>	99.635	1	3.0756	4.3343	6.5014	7.2238	15.924
<sup>7</sup> N <sup>15</sup>	0.365	1/2	4.3142	6.0798	9.1197	10.1330	22.2925
<sup>8</sup> O <sup>17</sup>	0.037	5/2	5.772	8.134	12.201	13.557	29.825
<sup>9</sup> F <sup>19</sup>	100	1/2	40.0541	42.3537	63.5305	94.0769	206.9692
<sup>14</sup> Si <sup>29</sup>	4.70	1/2	8.4578	11.9191	17.8787	19.8652	43.7035
<sup>15</sup> P <sup>31</sup>	100	1/2	17.235	24.288	36.433	40.481	89.057
<sup>16</sup> S <sup>33</sup>	0.76	3/2	3.2654	4.6018	6.9026	7.6696	16.8731
<sup>16</sup> S <sup>35 b</sup>	—	3/2	5.08	7.16	10.74	11.932	26.250
<sup>17</sup> Cl <sup>35</sup>	75.53	3/2	4.1717	5.8790	8.8184	9.7983	21.5562
<sup>17</sup> Cl <sup>36 b</sup>	—	2	4.8931	6.8956	10.3434	11.4927	25.2838
<sup>35</sup> Br <sup>76 b</sup>	—	1	4.18	5.89	8.84	9.82	21.60
<sup>35</sup> Br <sup>79</sup>	50.54	3/2	10.667	15.032	22.549	25.054	55.119
<sup>35</sup> Br <sup>81</sup>	49.46	3/2	11.498	16.204	24.305	27.006	59.413
<sup>74</sup> W <sup>183</sup>	14.40	1/2	1.7716	2.4966	3.7449	4.1610	9.1543

Isotope	Field Value <sup>a</sup> (kg) at Frequency of			Relative Sensitivity		Magnetic Moment (eh/4πM <sub>c</sub> )	Electric Quadrupole Moment <sup>c</sup> (barns)
	4 MHz	10 MHz	16 MHz	Constant H	Constant ν		
<sup>1</sup> H <sup>1</sup>	0.940	2.349	3.758	1.00	1.00	2.79278	—
<sup>1</sup> H <sup>2</sup>	6.120	15.30	24.48	9.65 × 10 <sup>-3</sup>	0.409	0.85742	0.0028
<sup>1</sup> H <sup>3 b</sup>	0.881	2.202	3.523	1.21	1.07	2.9789	—
<sup>6</sup> C <sup>13</sup>	3.736	9.341	14.946	0.0159	0.252	0.7024	—
<sup>7</sup> N <sup>14</sup>	13.01	32.51	52.02	1.01 × 10 <sup>-3</sup>	0.193	0.4036	0.01
<sup>7</sup> N <sup>15</sup>	9.272	23.18	37.09	1.04 × 10 <sup>-3</sup>	0.101	-0.2831	—
<sup>8</sup> O <sup>17</sup>	6.93	17.3	27.7	0.0291	1.58	-1.8937	-0.026
<sup>9</sup> F <sup>19</sup>	0.999	2.497	3.994	0.834	0.941	2.6288	—
<sup>14</sup> Si <sup>29</sup>	4.729	11.82	18.92	7.84 × 10 <sup>-3</sup>	0.199	-0.55477	—
<sup>15</sup> P <sup>31</sup>	2.321	5.802	9.284	0.0665	0.405	1.1317	—
<sup>16</sup> S <sup>33</sup>	12.25	30.62	49.0	2.26 × 10 <sup>-3</sup>	0.384	0.6533	-0.055
<sup>16</sup> S <sup>35 b</sup>	7.87	19.7	31.5	8.50 × 10 <sup>-3</sup>	0.597	1.00	0.04
<sup>17</sup> Cl <sup>35</sup>	9.588	23.97	38.35	4.72 × 10 <sup>-3</sup>	0.490	0.82183	-0.079
<sup>17</sup> Cl <sup>36 b</sup>	0.175	20.44	32.70	0.0122	0.920	1.285	-0.017
<sup>35</sup> Br <sup>76 b</sup>	9.6	24	38	2.52 × 10 <sup>-3</sup>	0.26	±0.548	±0.25
<sup>35</sup> Br <sup>79</sup>	3.750	9.375	15.00	0.0794	1.26	2.106	0.31
<sup>35</sup> Br <sup>81</sup>	3.479	8.697	13.92	0.0994	1.35	2.270	0.26
<sup>74</sup> W <sup>183</sup>	22.58	56.45	90.31	7.3 × 10 <sup>-5</sup>	0.042	0.117	—

<sup>a</sup> 1 kG = 10<sup>-10</sup> T, the corresponding SI unit.

<sup>b</sup> Nucleus is radioactive.

<sup>c</sup> 1 b = 10<sup>-23</sup> m<sup>2</sup>.

## GYROMAGNETIC RATIO OF SOME IMPORTANT NUCLEI

The following table lists the gyromagnetic ratio,  $\gamma$ , of some important nuclei that are probed in NMR spectroscopy.<sup>1-12</sup> The gyromagnetic ratio is the proportionality constant that correlates the magnetic moment ( $\mu$ ) and the angular momentum,  $\rho$ :  $\mu = \gamma\rho$ .

### REFERENCES

1. Carrington, A. and McLaughlin, A., *Introduction to Magnetic Resonance*, Harper and Row, New York, 1967.
2. Levine, I.M., *Molecular Spectroscopy*, John Wiley & Sons, New York, 1975.
3. Becker, E.D., *High Resolution NMR: Theory and Chemical Applications*, Academic Press, New York, 1980.
4. Yoder, C.H. and Shaeffer, C.D., *Introduction to Multinuclear NMR*, Benjamin/Cummings, Menlo Park, CA, 1987.
5. Silverstein, R.M. and Webster F.X., *Spectrometric Identification of Organic Compounds*, 6th ed., John Wiley & Sons, New York, 1998.
6. Rahman, A.-U., *Nuclear Magnetic Resonance*, Springer-Verlag, New York, 1986.
7. Kitamaru, R., *Nuclear Magnetic Resonance: Principles and Theory*, Elsevier Science, Amsterdam, 1990.
8. Lambert, J.B., Holland, L.N., and Mazzola, E.P., *Nuclear Magnetic Resonance Spectroscopy: Introduction to Principles, Applications and Experimental Methods*, Prentice Hall, Englewood Cliffs, NJ, 2003.
9. Bovey, F.A. and Mirau, P.A., *Nuclear Magnetic Resonance Spectroscopy*, 2nd ed., Academic Press, 1988.
10. Hore, P.J. and Hore, P.J., *Nuclear Magnetic Resonance*, Oxford University Press, Oxford, 1995.
11. Nelson, J.H., *Nuclear Magnetic Resonance Spectroscopy*, 2nd ed., John Wiley & Sons, New York, 2003.
12. Gunther, H., *NMR Spectroscopy: Basic Principles, Concepts and Applications in Chemistry*, John Wiley & Sons, New York, 2003.

Gyromagnetic Ratio of Some Important Nuclei	
Nucleus	$\gamma$
$^1_1\text{H}^1$	5.5856
$^2_1\text{H}^2$	0.8574
$^3_1\text{H}^3$	5.9575
$^7_3\text{Li}^7$	2.1707
$^{10}_5\text{B}^{10}$	0.6002
$^{11}_5\text{B}^{11}$	1.7920
$^{13}_6\text{C}^{13}$	1.4044
$^{14}_7\text{N}^{14}$	0.4035
$^{15}_7\text{N}^{15}$	-0.5660
$^{17}_8\text{O}^{17}$	-0.7572
$^{19}_9\text{F}^{19}$	5.2545
$^{29}_{14}\text{Si}^{29}$	-1.1095
$^{23}_{11}\text{Na}^{23}$	1.4774
$^{31}_{15}\text{P}^{31}$	2.2610
$^{33}_{16}\text{S}^{33}$	0.4284
$^{35}_{17}\text{Cl}^{35}$	0.5473
$^{37}_{17}\text{Cl}^{37}$	0.4555
$^{39}_{19}\text{K}^{39}$	0.2607
$^{79}_{35}\text{Br}^{79}$	1.3993
$^{81}_{35}\text{Br}^{81}$	1.5084
$^{183}_{74}\text{W}^{183}$	0.2324

## CLASSIFICATION OF IMPORTANT QUADRUPOLAR NUCLEI ACCORDING TO NATURAL ABUNDANCE AND MAGNETIC STRENGTH

The following table classifies important quadrupolar nuclei according to their natural abundance and relative magnetic strength.<sup>1</sup> The magnetic strength, while not a commonly recognized physical parameter, is defined as a matter of convenience for classification of nuclei in NMR. It is defined as follows:

Strong     $\gamma/10^7 > 2.5 \text{ rad T}^{-1}\text{sec}^{-1}$   
Medium    $10 \text{ rad T}^{-1}\text{sec}^{-1} > \gamma/10^7 > 2.5 \text{ rad T}^{-1}\text{sec}^{-1}$   
Weak      $\gamma/10^7 < 2.5 \text{ rad T}^{-1}\text{sec}^{-1}$

where the flux density in units of tesla (T) and rad refers to  $2\pi$ . In NMR, one can write:

$$2\pi f = \gamma B$$

where  $f$  is the resonant frequency,  $\gamma$  is the gyromagnetic ratio, and  $B$  is the flux density. Thus, for the proton,  $\gamma/2\pi = 43 \text{ MHz/T}$ , resulting in a value of  $\gamma/10^7 = 4.3 \text{ rad T}^{-1}\text{sec}^{-1}$ , and therefore medium magnetic strength.

The less favorable nuclei for a given element are listed in brackets.

## REFERENCES

1. Harris, R.K. and Mass, B.E., *NMR and the Periodic Table*, Academic Press, London, 1978.

**Classification of Important Quadrupolar Nuclei According to Natural Abundance and Magnetic Strength**

Magnetic Strength	Natural Abundance		
	High (>90%)	Medium	Low (<10%)
Strong	<sup>7</sup> Li		
Medium	<sup>9</sup> Be, <sup>23</sup> Na, <sup>27</sup> Al, <sup>45</sup> Sc, <sup>51</sup> V, <sup>55</sup> Mn, <sup>59</sup> Co, <sup>75</sup> As, <sup>93</sup> Nb, <sup>115</sup> In, <sup>127</sup> I, <sup>133</sup> Cs, <sup>181</sup> Ta, <sup>209</sup> Bi	[ <sup>10</sup> B], <sup>11</sup> B, <sup>35</sup> Cl, <sup>63</sup> Cu, <sup>65</sup> Cu, [ <sup>69</sup> Ga], <sup>71</sup> Ga, [ <sup>79</sup> Br], <sup>81</sup> Br, [ <sup>85</sup> Rb], <sup>87</sup> Rb, <sup>121</sup> Sb, [ <sup>123</sup> Sb], <sup>137</sup> Ba, <sup>139</sup> La, [ <sup>185</sup> Re], <sup>187</sup> Re	<sup>2</sup> H, <sup>6</sup> Li, <sup>17</sup> O, <sup>21</sup> Ne, [ <sup>113</sup> In], [ <sup>135</sup> Ba]
Weak	<sup>14</sup> N, <sup>39</sup> K	<sup>25</sup> Mg, <sup>37</sup> Cl, <sup>83</sup> Kr, <sup>95</sup> Mo, <sup>131</sup> Xe, <sup>189</sup> Os, <sup>201</sup> Hg	<sup>33</sup> S, [ <sup>41</sup> K], <sup>43</sup> Ca, <sup>47</sup> Ti, <sup>49</sup> Ti, <sup>53</sup> Cr, <sup>67</sup> Zn, <sup>73</sup> Ge, <sup>87</sup> Sr, [ <sup>97</sup> Mo]

## CHEMICAL SHIFT RANGES OF SOME NUCLEI

The following table gives an approximate chemical shift range (in ppm) for some of the most popular nuclei. The range is established by the shifts recorded for the most common compounds.<sup>1-11</sup>

### REFERENCES

1. Yoder, C.H. and Schaeffer, C.D., Jr., *Introduction to Multinuclear NMR*, Benjamin/Cummings Publishing Co., Menlo Park, CA, 1987.
2. Silverstein, R.M., Bassler, G.C., and Morrill, T.C., *Spectrometric Identification of Organic Compounds*, 5th ed., John Wiley & Sons, New York, 1991.
3. Harris, R.U. and Mann, B.E., *NMR and the Periodic Table*, Academic Press, London, 1978.
4. Silverstein, R.M. and Webster F.X., *Spectrometric Identification of Organic Compounds*, 6th ed., John Wiley & Sons, New York, 1998.
5. Gunther, H., *NMR Spectroscopy: Basic Principles, Concepts and Applications in Chemistry*, John Wiley & Sons, New York, 2003.
6. Kitamaru, R., *Nuclear Magnetic Resonance: Principles and Theory*, Elsevier Science, New York, 1990.
7. Lambert, J.B., Holland, L.N., and Mazzola, E.P., *Nuclear Magnetic Resonance Spectroscopy: Introduction to Principles, Applications and Experimental Methods*, Prentice Hall, Englewood Cliffs, NJ, 2003.
8. Bovey, F.A. and Mirau, P.A., *Nuclear Magnetic Resonance Spectroscopy*, 2nd ed., Academic Press, New York, 1988.
9. Harris, R.K. and Mann, B.E., *NMR and the Periodic Table*, Academic Press, London, 1978.
10. Hore, P.J. and Hore, P.J., *Nuclear Magnetic Resonance*, Oxford University Press, Oxford, 1995.
11. Nelson, J.H., *Nuclear Magnetic Resonance Spectroscopy*, 2nd ed., John Wiley & Sons, New York, 2003.

Chemical Shift Ranges of Some Nuclei

Nucleus	Chemical Shift Range, ppm	Nucleus	Chemical Shift Range, ppm
<sup>1</sup> H	15	<sup>29</sup> Si	400
<sup>7</sup> Li	10	<sup>31</sup> P	700
<sup>11</sup> B	200	<sup>33</sup> S	600
<sup>13</sup> C	250	<sup>35</sup> Cl	820
<sup>15</sup> N	930	<sup>39</sup> K	60
<sup>17</sup> O	700	<sup>59</sup> Co	14,000
<sup>19</sup> F	800	<sup>119</sup> Sn	2000
<sup>23</sup> Na	15	<sup>133</sup> Cs	150
<sup>27</sup> Al	270	<sup>207</sup> Pb	10,000

## REFERENCE STANDARDS FOR SELECTED NUCLEI

The following table lists the most popular reference standards used when NMR spectra of various nuclei are measured. The standards should be inert, soluble in a variety of solvents, and, preferably, produce one singlet peak that appears close to the lowest-frequency end of the chemical shift range. When NMR data are provided, it is always necessary to specify the reference standard employed.<sup>1-6</sup>

## REFERENCES

1. Yoder, C.H. and Schaeffer, C.D., Jr., *Introduction to Multinuclear NMR*, Benjamin/Cummings Publishing Co., Menlo Park, CA, 1987.
2. Duthaler, R.O. and Roberts, J.D., Steric and electronic effects on <sup>15</sup>N chemical shifts of piperidine and decahydroquinoline hydrochlorides, *J. Am. Chem. Soc.*, 100, 3889, 1978.
3. Grim, S.O. and Yankowsky, A.W., On the phosphorus-31 chemical shifts of substituted triarylphosphines, *Phosphorus Sulfur*, 3, 191, 1977.
4. Lambert, J.B., Shurrell, H.F., Verbit, L., Cooks, R.G., and Stout, G.H., *Organic Structural Analysis*, MacMillan, New York, 1976.
5. Gunther, H., *NMR Spectroscopy: Basic Principles, Concepts and Applications in Chemistry*, John Wiley & Sons, New York, 2003.
6. Abraham, R.J., Fisher, J., and Loftus, P., *Introduction to NMR Spectroscopy*, John Wiley & Sons, New York, 1988.

Reference Standards for Selected Nuclei

Nucleus	Name	Formula
<sup>1</sup> H	Tetramethylsilane [TMS]	(CH <sub>3</sub> ) <sub>4</sub> Si
	3-(Trimethylsilyl)-1-propanesulfonic acid, sodium salt [DSS] <sup>a</sup>	(CH <sub>3</sub> ) <sub>3</sub> Si(CH <sub>2</sub> ) <sub>3</sub> SO <sub>3</sub> Na
	3-(Trimethylsilyl)-propanoic acid, d <sub>4</sub> , sodium salt [TSP]	(CH <sub>3</sub> ) <sub>3</sub> Si(CD <sub>2</sub> ) <sub>3</sub> CO <sub>2</sub> Na
<sup>2</sup> H	Deuterated chloroform [chloroform-d]	CDCl <sub>3</sub>
<sup>11</sup> B	Boric acid	H <sub>3</sub> BO <sub>3</sub>
	Boron trifluoride etherate	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O·BF <sub>3</sub>
	Boron trichloride	BCl <sub>3</sub>
<sup>13</sup> C	Tetramethylsilane [TMS]	(CH <sub>3</sub> ) <sub>4</sub> Si
<sup>15</sup> N	Ammonium nitrate	NH <sub>4</sub> NO <sub>3</sub>
	Ammonia	NH <sub>3</sub>
	Nitromethane	CH <sub>3</sub> NO <sub>2</sub>
	Nitric acid	HNO <sub>3</sub>
	Tetramethylammonium chloride	(CH <sub>3</sub> ) <sub>4</sub> NCl
<sup>17</sup> O	Water	H <sub>2</sub> O
<sup>19</sup> F	Trichlorofluoromethane [Freon 11, R-11]	CCl <sub>3</sub> F
	Hexafluorobenzene	C <sub>6</sub> F <sub>6</sub>
<sup>31</sup> P	Trimethylphosphite [methyl phosphite]	(CH <sub>3</sub> O) <sub>3</sub> P
	Phosphoric acid (85%)	H <sub>3</sub> PO <sub>4</sub>
<sup>35</sup> Cl	Sodium chloride	NaCl
<sup>59</sup> Co	Cobalt (III) hexacyanide anion	[Co(CN) <sub>6</sub> ] <sup>-3</sup>
<sup>119</sup> Sn	Tetramethyltin	(CH <sub>3</sub> ) <sub>4</sub> Sn
<sup>195</sup> Pt	Platinum (IV) hexacyanide	[Pt(CN) <sub>6</sub> ] <sup>-2</sup>
	Dihydrogen platinum (IV) hexachloride	H <sub>2</sub> PtCl <sub>6</sub>
<sup>183</sup> W	Sodium tungstate (external)	Na <sub>2</sub> WO <sub>4</sub>

<sup>a</sup> For aqueous solutions (known also as water-soluble TMS or 2,2-dimethyl-2-silapentane-5-sulfonate).

## <sup>1</sup>H AND <sup>13</sup>C CHEMICAL SHIFTS OF USEFUL SOLVENTS FOR NMR MEASUREMENTS

The following table lists the expected <sup>1</sup>H( $\delta^H$ ) and <sup>13</sup>C( $\delta^C$ ) chemical shifts for various useful NMR solvents in parts per million (ppm). The table also includes the liquid temperature range (°C) and dielectric constants of these solvents. Slight changes may occur with changes in concentration.

### REFERENCES

1. Silverstein, R.M., Bassler, G.C., and Morrill, T.C., *Spectrometric Identification of Organic Compounds*, 5th ed., John Wiley & Sons, New York, 1991.
2. Rahman, A.-U., *Nuclear Magnetic Resonance: Basic Principles*, Springer-Verlag, New York, 1986.
3. Abraham, R.J., Fisher, J., and Loftus, P., *Introduction of NMR Spectroscopy*, John Wiley & Sons, Chichester, U.K., 1988.

<sup>1</sup>H and <sup>13</sup>C Chemical Shifts of Useful Solvents for NMR Measurements

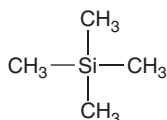
Solvent	Formula	Liquid Temperature Range (°C)	Dielectric Constant, $\epsilon$	Chemical Shifts	
				$\delta_H$ (ppm)	$\delta_C$ (ppm)
Acetone-d <sub>6</sub>	(CD <sub>3</sub> ) <sub>2</sub> CO	−95 to 56	20.7	2.17	29.2, 204.1
Acetonitrile-d <sub>3</sub>	CD <sub>3</sub> CN	−44 to 82	37.5	2.00	1.3, 117.7
Benzene-d <sub>6</sub>	C <sub>6</sub> D <sub>6</sub>	6 to 80	2.284	7.27	128.4
Carbon disulfide	CS <sub>2</sub>	−112 to 46	2.641	—	192.3
Carbon tetrachloride	CCl <sub>4</sub>	−23 to 77	2.238	—	96.0
Chloroform-d <sub>3</sub>	CDCl <sub>3</sub>	−64 to 61	4.806	7.25	76.9
Cyclohexane-d <sub>12</sub>	C <sub>6</sub> D <sub>12</sub>	6 to 81	2.023	1.43	27.5
Dichloromethane-d <sub>2</sub>	CD <sub>2</sub> Cl <sub>2</sub>	−95 to 40	9.08	5.33	53.6
Difluorobromochloromethane	CF <sub>2</sub> BCl	−140 to −25	—	—	109.2
Dimethylformamide-d <sub>7</sub>	DCON(CD <sub>3</sub> ) <sub>2</sub>	−60 to 153	36.7	2.9, 3.0, 8.0	31, 36, 132.4
Dimethylsulfoxide-d <sub>6</sub>	(CD <sub>3</sub> ) <sub>2</sub> SO	19 to 189	46.7	2.62	39.6
1,4-Dioxane-d <sub>8</sub>	C <sub>4</sub> D <sub>8</sub> O <sub>2</sub>	12 to 101	2.209	3.7	67.4
HMPA		7 to 233	30.0	2.60	36.8
Methanol-d <sub>4</sub>	CD <sub>3</sub> OD	−98 to 65	32.63	3.4, 4.8 <sup>a</sup>	49.3
Nitrobenzene	C <sub>6</sub> D <sub>5</sub> NO <sub>2</sub>	6 to 211	34.8	8.2, 7.6, 7.5	149, 134, 129, 124
Nitromethane-d <sub>3</sub>	CD <sub>3</sub> NO <sub>2</sub>	−29 to 101	35.87	4.33	57.3
Pyridine-d <sub>5</sub>	C <sub>5</sub> D <sub>5</sub> N	−42 to 115	123	7.0, 7.6, 8.6	124, 136, 150
1,1,2,2-Tetrachloroethane-d <sub>2</sub>	CD <sub>2</sub> ClCD <sub>2</sub> Cl	−44 to 146	8.2	5.94	75.5
Tetrahydrofuran-d <sub>8</sub>	C <sub>4</sub> D <sub>8</sub> O	−108 to 66	7.54	1.9, 3.8	25.8, 67.9
1,2,4-Trichlorobenzene	C <sub>6</sub> D <sub>3</sub> Cl <sub>3</sub>	17 to 214	3.9	7.1, 7.3, 7.4	133.3, 132.8, 130.7, 130.0, 127.6
Trichlorofluoromethane	CFCl <sub>3</sub>	−111 to 24	2.3	—	117.6
Vinyl chloride-d <sub>3</sub>	CD <sub>2</sub> =CDCl	−154 to −13	—	5.4, 5.5, 6.3	126, 117
Trifluoroacetic acid, d	CF <sub>3</sub> COOD	−15 to 72	8.6	11.3 <sup>a</sup>	114.5, 116.5
Water-d <sub>2</sub>	D <sub>2</sub> O	0 to 100	78.5	4.7	—

<sup>a</sup> Variable with concentration.



## PROTON NMR ABSORPTION OF MAJOR CHEMICAL FAMILIES

The following tables give the region of the expected nuclear magnetic resonance absorptions of major chemical families. These absorptions are reported in the dimensionless units of parts per million (ppm) vs. the standard compound tetramethylsilane (TMS), which is recorded as 0.0 ppm:



The use of this unit of measure makes the chemical shifts independent of the applied magnetic field strength or the radio frequency. For most proton NMR spectra, the protons in TMS are more shielded than almost all other protons. The chemical shift in this dimensionless unit system is then defined by

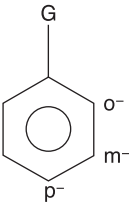
$$\delta = \frac{\nu_s - \nu_r}{\nu_r} \times 10^6$$

where  $\nu_s$  and  $\nu_r$  are the absorption frequencies of the sample proton and the reference (TMS) protons (12, magnetically equivalent), respectively. In these tables, the protons whose proton NMR shifts are cited are indicated by an underline. For more detail concerning these conventions, refer to the general references below.<sup>1-11</sup>

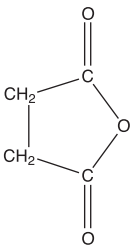
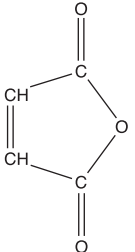



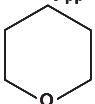
## REFERENCES

1. Silverstein, R.M. and Webster, F.X., *Spectrometric Identification of Organic Compounds*, 6th ed., Wiley, New York, 1998.
2. Rahman, A.-U., *Nuclear Magnetic Resonance*, Springer-Verlag, New York, 1986.
3. Gordon, A.J. and Ford, R.A., *The Chemist's Companion*, Wiley Interscience, New York, 1971.
4. Becker, E.D., *High Resolution NMR, Theory and Chemical Applications*, 2nd ed., Academic Press, New York, 1980.
5. Gunther, H., *NMR Spectroscopy: Basic Principles, Concepts and Applications in Chemistry*, Wiley, New York, 2003.
6. Kitamaru, R., *Nuclear Magnetic Resonance: Principles and Theory*, Elsevier Science, Amsterdam, 1990.
7. Lambert, J.B., Holland, L.N., and Mazzola, E.P., *Nuclear Magnetic Resonance Spectroscopy: Introduction to Principles, Applications and Experimental Methods*, Prentice Hall, Englewood Cliffs, NJ, 2003.
8. Bovey, F.A. and Mirau, P.A., *Nuclear Magnetic Resonance Spectroscopy*, 2nd ed., Academic Press, New York, 1988.
9. Hore, P.J. and Hore, P.J., *Nuclear Magnetic Resonance*, Oxford University Press, Oxford, 1995.
10. Nelson, J.H., *Nuclear Magnetic Resonance Spectroscopy*, 2nd ed., Wiley, New York, 2003.
11. Abraham, R.J., Fisher, J., and Loftus, P., *Introduction to NMR Spectroscopy*, Wiley, New York, 1988.

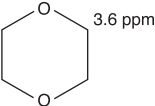
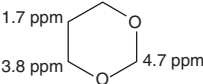
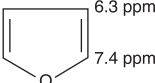
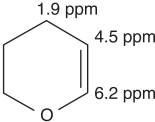
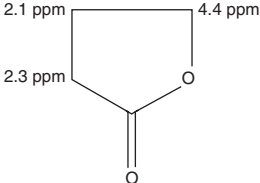
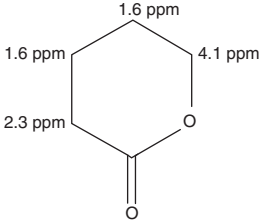
## Hydrocarbons

Family	$\delta$ of Protons Underlined or Indicated	
Alkanes	$\underline{\text{CH}_3}\text{-R}$ ~0.8 ppm $\text{-}\underline{\text{CH}_2}\text{-R}$ ~1.1 ppm $\text{>}\underline{\text{CH}}\text{-R}$ ~1.4 ppm (Cyclopropane, 0.2 ppm)	
Alkenes	$\underline{\text{CH}_3}\text{-C=C<}$ ~1.6 ppm $\text{-}\underline{\text{CH}_2}\text{-C=C<}$ ~2.1 ppm $\text{>}\underline{\text{CH}}\text{-C=C<}$ ~2.5 ppm $\text{>C=}\underline{\text{CH}}$ 4.2–6.2 ppm	$\underline{\text{CH}_3}\text{-C=C=C<}$ ~1.0 ppm $\text{-}\underline{\text{CH}_2}\text{-C=C=C<}$ ~1.4 ppm $\text{>}\underline{\text{CH}}\text{-C=C=C<}$ ~1.8 ppm
Alkynes	$\underline{\text{CH}_3}\text{-C}\equiv\text{C-}$ ~1.7 ppm $\text{-}\underline{\text{CH}_2}\text{-C}\equiv\text{C-}$ ~2.2 ppm $\text{>}\underline{\text{CH}}\text{-C}\equiv\text{C-}$ ~2.7 ppm $\text{R-C}\equiv\text{C-}\underline{\text{H}}$ ~2.4 ppm	$\underline{\text{CH}_3}\text{-C}\equiv\text{C-}$ ~1.2 ppm $\text{>}\underline{\text{CH}_2}\text{-C}\equiv\text{C-}$ ~1.5 ppm $\text{>}\underline{\text{CH}}\text{-C}\equiv\text{C-}$ ~1.8 ppm
Aromatics	$\text{C}_6\text{H}_5\text{-G}$ <div style="text-align: center;">  </div> <p>When <math>\underline{\text{G}}</math>=electron withdrawing (e.g., <math>\text{&gt;C=O}</math>, <math>\text{-NO}_2</math>, <math>\text{-C}\equiv\text{N}</math>), <i>o</i>- and <i>p</i>-hydrogens relative to <math>\text{-G}</math> are closer to 8.5 ppm (more downfield)</p>	Range: 8.5–6.9 ppm  <p>When <math>\underline{\text{G}}</math>=electron donating (e.g., <math>\text{-NH}_2</math>, <math>\text{-OH}</math>, <math>\text{-OR}</math>, <math>\text{-R}</math>), <i>o</i>- and <i>p</i>-hydrogens relative to <math>\text{-G}</math> are closer to 6.9 ppm (more upfield)</p>

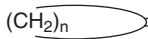
## Organic Oxygen Compounds

Family	Approximate $\delta$ of Protons Underlined or Indicated					
Alcohols	<u>CH<sub>3</sub></u> -OH	3.2 ppm	R <u>CH<sub>2</sub></u> -OH	3.4 ppm	R <sub>2</sub> <u>CH</u> -OH	3.6 ppm
	<u>CH<sub>3</sub></u> -C-OH	1.2 ppm	R <u>CH<sub>2</sub></u> -C-OH	1.5 ppm	R <sub>2</sub> <u>CH</u> -C-OH	1.8 ppm
	R-O- <u>H</u> (1–5 ppm — depending on concentration)					
Aldehydes	<u>CH<sub>3</sub></u> -CHO	2.2 ppm	R <u>CH<sub>2</sub></u> -CHO	2.4 ppm	R <sub>2</sub> <u>CH</u> -CHO	2.5 ppm
	<u>CH<sub>3</sub></u> -C-CHO	1.1 ppm	R <u>CH<sub>2</sub></u> -C-CHO	1.6 ppm		
Amides	See Organic Nitrogen Compounds					
Anhydrides, acyclic	<u>CH<sub>3</sub></u> -C(=O)O-	1.8 ppm	R <u>CH<sub>2</sub></u> -C(=O)O-	2.1 ppm	R <sub>2</sub> <u>CH</u> -C(=O)O-	2.3 ppm
	<u>CH<sub>3</sub></u> -C-C(=O)O-	1.2 ppm	R <u>CH<sub>2</sub></u> -C-C(=O)O-	1.8 ppm	R <sub>2</sub> <u>CH</u> -C-C(=O)O-	2.0 ppm
Anhydrides, cyclic	3.0 ppm				7.1 ppm	
						
Carboxylic acids	<u>CH<sub>3</sub></u> -COOH	2.1 ppm	R <u>CH<sub>2</sub></u> -COOH	2.3 ppm	R <sub>2</sub> <u>CH</u> -COOH	2.5 ppm
	<u>CH<sub>3</sub></u> -C-COOH	1.1 ppm	R- <u>CH<sub>2</sub></u> -C-COOH	1.6 ppm	R <sub>2</sub> <u>CH</u> -C-COOH	2.0 ppm
	R-COO- <u>H</u> 11–12 ppm					
Cyclic ethers	Oxacyclopropane (oxirane)					
			2.5 ppm			
	Oxacyclobutane (oxetane)					
			2.7 ppm 4.7 ppm			
Oxacyclopentane (tetrahydrofuran)						
			1.9 ppm 3.8 ppm			
Oxacyclohexane (tetrahydropyran)						
			1.6 ppm 1.6 ppm 3.6 ppm			

**Organic Oxygen Compounds (continued)**

Family	Approximate $\delta$ of Protons Underlined or Indicated		
1,4-Dioxane			
1,3-Dioxane			
Furan			
Dihydropyran			
Epoxides	See Cyclic Ethers		
Esters	$\text{CH}_3\text{--COOR}$ R = alkyl 1.9 ppm R = aryl 2.0 ppm	$\text{RCH}_2\text{--COOR}$ 2.1 ppm 2.2 ppm	$\text{R}_2\text{CH--COOR}$ 2.3 ppm 2.4 ppm
	$\text{CH}_3\text{--C--COOR}$ 1.1 ppm $\text{CH}_3\text{--OOC--R}$ 3.6 ppm $\text{CH}_3\text{--C--OOC--R}$ 1.3 ppm	$\text{RCH}_2\text{--C--COOR}$ 1.7 ppm $\text{RCH}_2\text{--OOC--R}$ 4.1 ppm $\text{RCH}_2\text{--C--OOC--R}$ 1.6 ppm	$\text{R}_2\text{CH--C--COOR}$ 1.9 ppm $\text{R}_2\text{CH--OOC--R}$ 4.8 ppm $\text{R}_2\text{CH--C--OOC--R}$ 1.8 ppm
Cyclic			
			
Ethers	R = alkyl R = aryl	$\text{CH}_3\text{--O--R}$ 3.2 ppm 3.9 ppm	$\text{RCH}_2\text{--O--R}$ 3.4 ppm 4.1 ppm
	R = alkyl R = aryl	$\text{CH}_3\text{--C--O--R}$ 1.2 ppm 1.3 ppm	$\text{RCH}_2\text{--C--O--R}$ 1.5 ppm 1.6 ppm
			$\text{R}_2\text{CH--O--R}$ 3.6 ppm 4.5 ppm
			$\text{R}_2\text{CH--C--O--R}$ 1.8 ppm 2.0 ppm

# Organic Oxygen Compounds (continued)

Family	Approximate $\delta$ of Protons Underlined		
Isocyanates	See Nitrogen Compounds		
Ketones	$\underline{\text{CH}_3}\text{-C(=O)-}$	$\text{R}\underline{\text{CH}_2}\text{-C(=O)-}$	$\text{R}_2\underline{\text{CH}}\text{-C(=O)-}$
	1.9 ppm R = alkyl	2.1 ppm	2.3 ppm
	2.4 ppm R = aryl	2.7 ppm	3.4 ppm
	$\underline{\text{CH}_3}\text{-C(=O)-}$	$\text{R}\underline{\text{CH}_2}\text{-C(=O)-}$	$\text{R}_2\underline{\text{CH}}\text{-C(=O)-}$
	1.1 ppm R = alkyl	1.6 ppm	2.0 ppm
	1.2 ppm R = aryl	1.6 ppm	2.1 ppm
	Cyclic ketones (n = number of ring carbons)		
	$(\text{CH}_2)_n$  $\alpha$ -hydrogens 2.0–2.3 ppm (n > 5) 3.0 ppm (n = 4) 1.7 ppm (n = 3) $\beta$ -hydrogens 1.9–1.5 ppm		
Lactones	See Esters, Cyclic		
Nitro compounds	See Organic Nitrogen Compounds		
Phenols	$\text{Ar-O-}\underline{\text{H}}$ 9–10 ppm (Ar = aryl)		

## ORGANIC NITROGEN COMPOUNDS

### Amides

$\delta$ of Proton(s) (Underlined)	Primary $R-C(=O)NH_2$ $\delta$ , ppm	Secondary $R-C(=O)NHR_1$ $\delta$ , ppm	Tertiary $R-C(=O)NR_1R_2$ $\delta$ , ppm
1. N-substitution $R-C(=O)\underline{N}-H$	5–12	5–12	—
a. Alpha $-C(=O)N-\underline{CH}_3$	—	~2.9	~2.9
$-C(=O)N-\underline{CH}_2-$	—	~3.4	~3.4
$-C(=O)N-\underline{CH}-$	—	~3.8	~3.8
b. Beta $-C(=O)N-C-\underline{CH}_3$	~1.1	~1.1	~1.1
$-C(=O)N-C-\underline{CH}_2-$	~1.5	~1.5	~1.5
$-C(=O)N-C-\underline{CH}-$	~1.9	~1.9	~1.9
2. C-substitution			
a. Alpha $\underline{CH}_3-C(=O)N$	~1.9	~2.0	~2.1
$R\underline{CH}_2-C(=O)N$	~2.1	~2.1	~2.1
$R_2\underline{CH}-C(=O)N$	~2.2	~2.2	~2.2
b. Beta $\underline{CH}_3-C-C(=O)N$	~1.1	~1.1	~1.1
$\underline{CH}_2-C-C(=O)N$	~1.5	~1.5	~1.5
$\underline{CH}-C-C(=O)N$	~1.8	~1.8	~1.8

### Amines

$\delta$ of Proton(s) (Underlined)	Primary $R-NH_2$ $\delta$ , ppm	Secondary $RN-HR$ $\delta$ , ppm	Tertiary $RRRN$ $\delta$ , ppm
1. Alpha protons $>\underline{N}-CH_3$	~2.5	2.3–3.0	~2.2
$>\underline{N}-CH_2-$	~2.7	2.6–3.4	~2.4
$>\underline{N}-CH<$	~3.1	2.9–3.6	~2.8
2. Beta protons $>\underline{N}-C-CH_3$			~1.1
$>\underline{N}-C-CH_2-$			~1.4
$>\underline{N}-C-\underline{CH}<$			~1.7

### Cyano Compounds (Nitriles)

1. Alpha hydrogens $\delta$ , ppm $\underline{CH}_3-C\equiv N$ ~2.1 $-\underline{CH}_2-C\equiv N$ ~2.5 $>\underline{CH}-C\equiv N$ ~2.9	2. Beta hydrogens $\delta$ , ppm $\underline{CH}_3-C-C\equiv N$ ~1.2 $-\underline{CH}_2-C-C\equiv N$ ~1.6 $>\underline{CH}-C-C\equiv N$ ~2.0
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### Imides

1. Alpha hydrogens $\delta$ , ppm $\underline{CH}_3-C(=O)NHC(=O)-$ ~2.0 $\underline{CH}_2-C(=O)NHC(=O)-$ ~2.1 $\underline{CH}-C(=O)NHC(=O)-$ ~2.2	2. Beta hydrogens $\delta$ , ppm $\underline{CH}_3-C(=O)C-NH-C(=O)-$ ~1.2 $\underline{CH}_2-C(=O)C-NH-C(=O)-$ ~1.3 $\underline{CH}-C(=O)C-NH-C(=O)-$ ~1.4
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### Isocyanates

Alpha hydrogens $\delta$ , ppm $\underline{CH}_3-N=C=O$ ~3.0 $-\underline{CH}_2-N=C=O$ ~3.3 $>\underline{CH}-N=C=O$ ~3.6
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Isocyanides (Isonitriles)	Isothiocyanates
Alpha hydrogens $\delta$ , ppm	Alpha hydrogens $\delta$ , ppm
$\text{CH}_3\text{-N=C}< \sim 2.9$	$\text{CH}_3\text{-N=C=S} \sim 3.4$
$\text{CH}_2\text{-N=C}< \sim 3.3$	$\text{CH}_2\text{-N=C=S} \sim 3.7$
$\text{CH-N=C}< \sim 4.9$	$\text{CH-N=C=S} \sim 4.0$

Nitriles $\delta$ , ppm
$\text{-CH}_2\text{-O-N=O} \sim 4.8$

Nitro Compounds $\delta$ , ppm					
<u>CH</u> <sub>3</sub> -NO <sub>2</sub>	~ 4.1	- <u>CH</u> <sub>2</sub> -NO <sub>2</sub>	~4.2	- <u>CH</u> -NO <sub>2</sub>	~4.4
<u>CH</u> <sub>3</sub> -C-NO <sub>2</sub>	~1.6	- <u>CH</u> <sub>2</sub> -C-NO <sub>2</sub>	~2.1	- <u>CH</u> -C-NO <sub>2</sub>	~2.5

## Organic Sulfur Compounds

Family	$\delta$ of Proton(s) Underlined	
Benzothiopyrans	$\text{sp}^3$ C-H ~3.3 ppm	$\text{sp}^2$ C-H 5.8–6.4 aromatic ~6.8
2H-1-	$\text{sp}^3$ C-H ~3.2 ppm	$\text{sp}^2$ C-H 5.9–6.3 aromatic ~6.9
4H-1-	$\text{sp}^3$ C-H 1.9–2.8 ppm	aromatic ~7.1
2,3,4H-1-		
Disulfides	$\text{CH}_3\text{-S-S-R}$ ~2.4 ppm	$\text{CH}_3\text{-C-S-S-R}$ ~1.2 ppm
	$\text{CH}_2\text{-S-S-R}$ ~2.7 ppm	$\text{CH}_2\text{-C-S-S-R}$ ~1.6 ppm
	$\text{CH-S-S-R}$ ~3.0 ppm	$\text{CH-C-S-S-R}$ ~2.0 ppm
Isothiocyanates	$\text{CH}_3\text{-N=C=S}$ ~2.4 ppm	
	$\text{-CH}_2\text{-N=C=S}$ ~2.7 ppm	
	$\text{>CH-N=C=S}$ ~3.0 ppm	
Mercaptans (thiols)	$\text{CH}_3\text{-S-H}$ ~2.1 ppm	$\text{CH}_3\text{-C-S-H}$ ~1.3 ppm
	$\text{-CH}_2\text{-S-H}$ ~2.6 ppm	$\text{-CH}_2\text{-C-S-H}$ ~1.6 ppm
	$\text{>CH-S-H}$ ~3.1 ppm	$\text{>CH-C-S-H}$ ~1.7 ppm
S-methyl salts	$+$	
	$\text{>S-CH}_3$ ~3.2 ppm	
Sulfates	$(\text{CH}_3\text{-O})_2\text{S(=O)}_2$ ~3.4 ppm	
Sulfides	$\text{CH}_3\text{-S-}$ 1.8–2.1 ppm	$\text{CH}_3\text{-CH}_2\text{-S-}$ 1.1–1.2 ppm
	$\text{R-CH}_2\text{-S-}$ 1.9–2.4 ppm	$\text{CH}_3\text{-CHR-S-}$ 0.8–1.2 ppm
	$\text{R-CHR-S-}$ 2.8–3.4 ppm	$\text{CH}_3\text{-CHAr-S-}$ 1.3–1.4 ppm
	$\text{Ar-CH}_2\text{-S-}$ 4.1–4.2 ppm	$\text{CH}_3\text{-CR}_2\text{-S-}$ 1.0 ppm
	$\text{Ar-CHR-S-}$ 3.6–4.2 ppm	$\text{Ar-CH}_2\text{-CHR-S-}$ 3.0–3.2 ppm
	$\text{Ar}_2\text{-CH-S-}$ 5.1–5.2 ppm	$\text{>C=C-CH}_2\text{-CHAr-S-}$ 2.4–2.6 ppm
		$\text{>C=C-CH}_2\text{-CAr}_2\text{-S-}$ 2.5 ppm
		$\text{R}_2\text{CH-CH}_2\text{-S-}$ 2.6–3.0 ppm
		$\text{Ar}_2\text{-CH-CH}_2\text{-S-}$ 4.0–4.2 ppm
		$\text{>C=C-CHR-CHAr-S-}$ 2.3–2.4 ppm
		$\text{>C=C-CHR-CAr}_2\text{-S-}$ 2.8–3.2 ppm
Sulfilimines	$\text{CH}_3(\text{R})\text{S=N-R}^2$ ~2.5 ppm	
Sulfonamides	$\text{CH}_3\text{-SO}_2\text{NH}_2$ ~3.0 ppm	
Sulfonates	$\text{CH}_3\text{-SO}_2\text{-OR}$ ~3.0 ppm	
Sulfones	$\text{CH}_3\text{-SO}_2\text{-R}^2$ ~2.6 ppm	
Sulfonic acids	$\text{CH}_3\text{-SO}_3\text{H}$ ~3.0 ppm	
Sulfoxides	$\text{CH}_3\text{-S(=O)R}$ ~2.5 ppm	
	$\text{-CH}_2\text{-S(=O)R}$ ~3.1 ppm	
Thiocyanates	$\text{CH}_3\text{-S-C}\equiv\text{N}$ ~2.7 ppm	
	$\text{-CH}_2\text{-S-C}\equiv\text{N}$ ~3.0 ppm	
	$\text{-CH-S-C}\equiv\text{N}$ ~3.3 ppm	
Thiols	See Mercaptans	

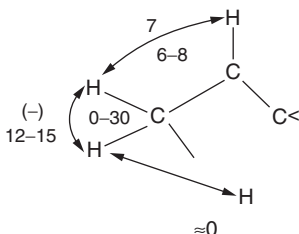
*Note:* Ar represents aryl.



## SOME USEFUL $^1\text{H}$ COUPLING CONSTANTS

This section gives the values of some useful proton NMR coupling constants (in Hz). The data are adapted with permission from the work of Dr. C.F. Hammer, Professor Emeritus, Chemistry Department, Georgetown University, Washington, D.C. 20057. The single numbers indicate a typical average, while in some cases the range is provided.

### 1. Freely rotating chains.



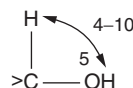
### 2. Alcohols with no exchange as in DMSO.

$1^\circ$  = triplet

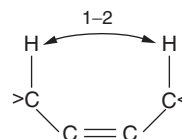
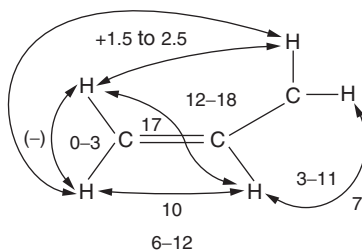
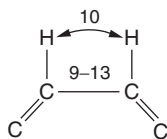
$2^\circ$  = doublet (broad)

$3^\circ$  = singlet

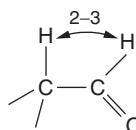
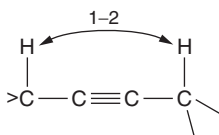
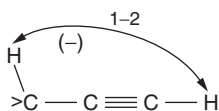
Upon addition of TFA, a sharp singlet results.



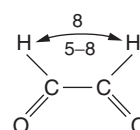
### 3. Alkenes



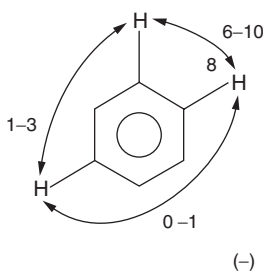
### 4. Alkynes



### 5. Aldehydes



### 6. Aromatic



## ADDITIVITY RULES IN $^{13}\text{C}$ NMR CORRELATION TABLES

The wide chemical shift range (~250 ppm) of  $^{13}\text{C}$  NMR is responsible for the considerable change of a chemical shift noted when a slight inductive, mesomeric, or hybridization neighboring change occurs. Following the various empirical correlations in  $^1\text{H}$  NMR,<sup>1-7</sup> D.W. Brown<sup>8</sup> has developed a short set of  $^{13}\text{C}$  NMR correlation tables. This section covers a part of those as adopted by Yoder and Schaeffer<sup>9</sup> and Clerk et al.<sup>10</sup> Refer to reference 8 for some accurate data on more complicated structures and look up the various references included in the literature cited below.<sup>1-17</sup>

## REFERENCES

1. Shoolery, J.N., *Varian Associates Technical Information Bulletin*, Vol. 2, No. 3, Palo Alto, CA, 1959.
2. Bell, H.M., Bowles, D.B., and Senese, F., Additive NMR chemical shift parameters for deshielded methine protons, *Org. Magn. Reson.*, 16, 285, 1981.
3. Matter, U.E., Pascual, C., Pretsch, E., Pross, A., Simon, W., and Sternhell, S., Estimation of the chemical shifts of olefinic protons using additive increments. II. Compilation of additive increments for 43 functional groups, *Tetrahedron*, 25, 691, 1969.
4. Matter, U.E., Pascual, C., Pretsch, E., Pross, A., Simon, W., and Sternhell, S., Estimation of the chemical shifts of olefinic protons using additive increments. III. Examples of utility in N.M.R. studies and the identification of some structural features responsible for deviations from additivity, *Tetrahedron*, 25, 2023, 1969.
5. Jeffreys, J.A.D., A rapid method for estimating NMR shifts for protons attached to carbon, *J. Chem. Educ.*, 56, 806, 1979.
6. Mikolajczyk, M., Grzejszczak, S., and Zatorski, A., Organosulfur compounds IX: NMR and structural assignments in  $\alpha,\beta$ -unsaturated sulfoxides using additive increments method, *Tetrahedron*, 32, 969, 1976.
7. Friedrich, E.C. and Runkle, K.G., Empirical NMR chemical shift correlations for methyl and methylene protons, *J. Chem. Educ.*, 61, 830, 1984.
8. Brown, D.W., A short set of  $^{13}\text{C}$ -NMR correlation tables, *J. Chem. Educ.*, 62, 209, 1985.
9. Yoder, C.H. and Schaeffer, C.D., Jr., *Introduction to Multinuclear NMR*, Benjamin/Cummings Publishing Co., Menlo Park, CA, 1987.
10. Clerk, J.T., Pretsch, E., and Seibl, J., *Structural Analysis of Organic Compounds by Combined Application of Spectroscopic Methods*, Elsevier, Amsterdam, 1981.
11. Silverstein, R.M. and Webster F.X., *Spectrometric Identification of Organic Compounds*, 6th ed., John Wiley & Sons, New York, 1998.
12. Gunther, H., *NMR Spectroscopy: Basic Principles, Concepts and Applications in Chemistry*, John Wiley & Sons, New York, 2003.
13. Kitamaru, R., *Nuclear Magnetic Resonance: Principles and Theory*, Elsevier Science, Amsterdam, 1990.
14. Lambert, J.B., Holland, L.N., and Mazzola, E.P., *Nuclear Magnetic Resonance Spectroscopy: Introduction to Principles, Applications and Experimental Methods*, Prentice Hall, Englewood Cliffs, NJ, 2003.
15. Bovey, F.A. and Mirau, P.A., *Nuclear Magnetic Resonance Spectroscopy*, 2nd ed., Academic Press, New York, 1988.
16. Harris, R.K. and Mann, B.E., *NMR and the Periodic Table*, Academic Press, London, 1978.
17. Nelson, J.H., *Nuclear Magnetic Resonance Spectroscopy*, 2nd ed., John Wiley & Sons, New York, 2003.

## Alkanes

The chemical shift (in ppm) of C<sup>i</sup> can be calculated from the following empirical equation:

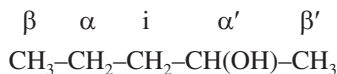
$$\Delta^i = -2.3 + \Sigma A_i$$

where  $\Sigma A_i$  is the sum of increments allowed for various substituents depending on their positions ( $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ ) relative to the <sup>13</sup>C in question and (−2.3) is the chemical shift for methane relative to tetramethylsilane (TMS).

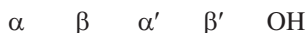
**<sup>13</sup>C Chemical Shift Increments for A, the Shielding Term  
for Alkanes and Substituted Alkanes<sup>9,10</sup>**

Substituent	Increments			
	$\alpha$	$\beta$	$\gamma$	$\delta$
>C– (sp <sup>3</sup> )	9.1	9.4	−2.5	0.3
>C=C< (sp <sup>2</sup> )	19.5	6.9	−2.1	0.4
−C≡C– (sp)	4.4	5.6	−3.4	−0.6
C <sub>6</sub> H <sub>5</sub>	22.1	9.3	−2.6	0.3
−F	70.1	7.8	−6.8	0.0
−Cl	31.0	10.0	−5.1	−0.5
−Br	18.9	11.0	−3.8	−0.7
−I	−7.2	10.9	−1.5	−0.9
−OH	49.0	10.1	−6.2	0.0
−OR	49.0	10.1	−6.2	0.0
−CHO	29.9	−0.6	−2.7	0.0
−COR	22.5	3.0	−3.0	0.0
−COOH	20.1	2.0	−2.8	0.0
−COO <sup>−</sup>	24.5	3.5	−2.5	0.0
−COCl	33.1	2.3	−3.6	0.0
−COOR	22.6	2.0	−2.8	0.0
−OOCR	5.5	6.5	−6.0	
−N<	28.3	11.3	−5.1	
−NH <sub>3</sub> <sup>+</sup>	26.0	7.5	−4.6	0.0
[>N<] <sup>+</sup>	30.7	5.4	−7.2	−1.4
−ONO	54.3	6.1	−6.5	−0.5
−NO <sub>2</sub>	61.6	3.1	−4.6	−1.0
−CON<	22.0	2.6	−3.2	−0.4
−NHCO–	31.3	8.3	−5.7	0.0
−C≡N	3.1	2.4	−3.3	−0.5
−NC	31.5	7.6	−3.0	0.0
−S–	10.6	11.4	−3.6	−0.4
−S–CO–	17.0	6.5	−3.1	0.0
−SO–	31.1	9.0	−3.5	0.0
−SO <sub>2</sub> Cl	54.5	3.4	−3.0	0.0
−SCN	23.0	9.7	−3.0	0.0
−C(=S)N–	33.1	7.7	−2.5	0.6
−C=NOH(syn)	11.7	0.6	−1.8	0.0
−C=NOH(anti)	16.1	4.3	−1.5	0.0
R <sub>1</sub> R <sub>2</sub> R <sub>3</sub> Sn	−5.2	4.0	−0.3	0.0
R <sub>1</sub> , R <sub>2</sub> , and R <sub>3</sub> = organic substituents				

Thus, the  $^{13}\text{C}$  shift for  $\text{C}^i$  in 2-pentanol is predicted to be

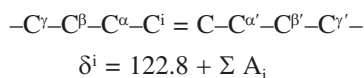


$$\delta^i = (-2.3) + [9.1 + 9.4 + 9.1 + 9.4 + 10.1] = 44.8 \text{ ppm}$$



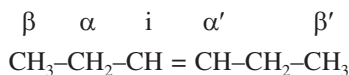
## Alkenes

For a simple olefin of the type

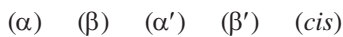


where  $A_\alpha = 10.6$ ,  $A_\beta = 7.2$ ,  $A_\gamma = -1.5$ ,  $A_{\alpha'} = -7.9$ ,  $A_{\beta'} = -1.8$ ,  $A_{\gamma'} = 1.5$ , and 122.8 is the chemical shift of the  $\text{sp}^2$  carbon in ethene.

If the olefin is in the *cis* configuration, an increment of  $-1.1$  ppm must be added. Thus, the  $^{13}\text{C}$  shift for C-3 in *cis*-3-hexene is predicted to be

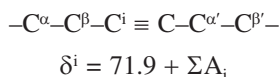


$$\delta^i = 122.8 + [10.6 + 7.2 - 1.5 - 7.9] + (-1.1) = 130.1 \text{ ppm}$$



## Alkynes

For a simple alkyne of the type

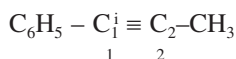


where increments A are given in the table below and 71.9 is the chemical shift of the  $\text{sp}$  carbon in acetylene.<sup>9</sup>

**$^{13}\text{C}$  Chemical Shift Increments for A, the Shielding Term for Alkynes**

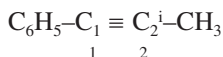
Substituents	Increments			
	$\alpha$	$\beta$	$\alpha'$	$\beta'$
C ( $\text{sp}^3$ )	6.9	4.8	-5.7	2.3
$-\text{CH}_3$	7.0		-5.7	
$-\text{CH}_2\text{CH}_3$	12.0		-3.5	
$-\text{CH}(\text{CH}_3)_2$	16.0		-3.5	
$-\text{CH}_2\text{OH}$	11.1		1.9	
$-\text{COCH}_3$	31.4		4.0	
$-\text{C}_6\text{H}_5$	12.7		6.4	
$-\text{CH}=\text{CH}_2$	10.0		11.0	
$-\text{Cl}$	-12.0		-15.0	

Thus, the  $^{13}\text{C}$  shift for C-1 in 1-phenyl propyne is predicted to be



$$\delta^i = 71.9 + 7.0 + 6.4 = 85.3 \text{ ppm}$$

while the  $^{13}\text{C}$  shift for C-2 in the same compound is predicted to be



$$\delta^i = 71.9 + 6.9 + 6.4 = 85.20 \text{ ppm}$$

## Benzenoid Aromatics

For a benzene derivative,  $\text{C}_6\text{H}_5\text{-X}$ , where X = substituent,

$$\delta^i = 128.5 + \Sigma A_i$$

where  $\Sigma A_i$  is the sum of increments given below and 128.5 is the chemical shift of benzene.<sup>9,10</sup>

**$^{13}\text{C}$  Chemical Shift Increments for A, the Shielding Term for Benzenoid Aromatics  $\text{X-C}_6\text{H}_5$ , where X = Substituent**

Substituent X	Increments			
	$\text{C}^i$	ortho	meta	para
$-\text{CH}_3$	9.3	0.8 <sup>9</sup> , 0.6 <sup>10</sup>	0.0	-2.9 <sup>9</sup> , -3.1 <sup>10</sup>
$-\text{CH}_2\text{CH}_3$	15.8 <sup>9</sup> , 15.7 <sup>10</sup>	-0.4 <sup>9</sup> , -0.6 <sup>10</sup>	-0.1	-2.6 <sup>9</sup> , -2.8 <sup>10</sup>
$-\text{CH}(\text{CH}_3)_2$	20.3 <sup>9</sup> , 20.1 <sup>10</sup>	-1.9 <sup>9</sup> , -2.0 <sup>10</sup>	0.1 <sup>9</sup> , 0.0 <sup>10</sup>	-2.4 <sup>9</sup> , -2.5 <sup>10</sup>
$-\text{C}(\text{CH}_3)_3$	22.4 <sup>9</sup> , 22.1 <sup>10</sup>	-3.1 <sup>9</sup> , -3.4 <sup>10</sup>	-0.2 <sup>9</sup> , 0.4 <sup>10</sup>	-2.9 <sup>9</sup> , -3.1 <sup>10</sup>
$-\text{CH}=\text{CH}_2$	7.6	-1.8	-1.8	-3.5
$-\text{C}\equiv\text{CH}$	-6.1	3.8	0.4	-0.2
$-\text{C}_6\text{H}_5$	13.0	-1.1	0.5	-1.0
$-\text{CHO}$	8.6 <sup>9</sup> , 9.0 <sup>10</sup>	1.3 <sup>9</sup> , 1.2 <sup>10</sup>	0.6 <sup>9</sup> , 1.2 <sup>10</sup>	5.5 <sup>9</sup> , 6.0 <sup>10</sup>
$-\text{COCH}_3$	9.1 <sup>9</sup> , 9.3 <sup>10</sup>	0.1 <sup>9</sup> , 0.2 <sup>10</sup>	0.0 <sup>9</sup> , 0.2 <sup>10</sup>	4.2
$-\text{CO}_2\text{H}$	2.1 <sup>9</sup> , 2.4 <sup>10</sup>	1.5 <sup>9</sup> , 1.6 <sup>10</sup>	0.0 <sup>9</sup> , -0.1 <sup>10</sup>	5.1 <sup>9</sup> , 4.8 <sup>10</sup>
$-\text{CO}_2^-$	7.6	0.8	0.0	2.8
$-\text{CO}_2\text{R}$	2.1	1.2	0.0	4.4
$-\text{CONH}_2$	5.4	-0.3	-0.9	5.0
$-\text{CN}$	-15.4 <sup>9</sup> , -16.0 <sup>10</sup>	3.6 <sup>9</sup> , 3.5 <sup>10</sup>	0.6 <sup>9</sup> , 0.7 <sup>10</sup>	3.9 <sup>9</sup> , 4.3 <sup>10</sup>
$-\text{Cl}$	6.2 <sup>9</sup> , 6.4 <sup>10</sup>	0.4 <sup>9</sup> , 0.2 <sup>10</sup>	1.3 <sup>9</sup> , 10.0 <sup>10</sup>	-1.9 <sup>9</sup> , -2.0 <sup>10</sup>
$-\text{OH}$	26.9	-12.7	1.4	-7.3
$-\text{O}-$	39.6 <sup>10</sup>	-8.2 <sup>10</sup>	1.9 <sup>10</sup>	-13.6 <sup>10</sup>
$-\text{OCH}_3$	31.4 <sup>9</sup> , 30.2 <sup>10</sup>	-14.4 <sup>9</sup> , -14.7 <sup>10</sup>	1.0 <sup>9</sup> , 0.9 <sup>10</sup>	-7.7 <sup>9</sup> , -8.1 <sup>10</sup>
$-\text{OC}_6\text{H}_5$	29.1	-9.5	0.3	-5.3
$-\text{OC}(=\text{O})\text{CH}_3$	23.0	-6.4	1.3	-2.3
$-\text{NH}_2$	18.7 <sup>9</sup> , 19.2 <sup>10</sup>	-12.4	1.3	-9.5
$-\text{NHCH}_3$	21.7 <sup>10</sup>	-16.2 <sup>10</sup>	0.7 <sup>10</sup>	-11.8 <sup>10</sup>
$-\text{N}(\text{CH}_3)_2$	22.4	-15.7	0.8	-11.8
$-\text{NO}_2$	20.0 <sup>9</sup> , 19.6 <sup>10</sup>	-4.8 <sup>9</sup> , -5.3 <sup>10</sup>	0.9 <sup>9</sup> , 0.8 <sup>10</sup>	5.8 <sup>9</sup> , 6.0 <sup>10</sup>
$-\text{SH}$	2.2	0.7	0.4	-3.1
$-\text{SCH}_3$	9.9 <sup>10</sup>	-2.0 <sup>10</sup>	0.1 <sup>10</sup>	-3.7 <sup>10</sup>
$-\text{SO}_3\text{H}$	15.0	-2.2	1.3	3.8

As an example, the  $^{13}\text{C}$  shift for the benzene carbon ( $\text{C}^i$ ) carrying the carbonyl in 3,5-dinitroacetophenone,  $\text{CH}_3\text{C}(=\text{O})(\text{C}_6\text{H}_3)(\text{NO}_2)_2$ , is predicted to be

$$\text{C}^i = 128.5 + 9.1 + 2(0.9) = 132.4 \text{ ppm}$$

## **$^{13}\text{C}$ NMR ABSORPTIONS OF MAJOR FUNCTIONAL GROUPS**

The table below lists the  $^{13}\text{C}$  chemical shift ranges (in ppm) with the corresponding functional groups in descending order. A number of typical simple compounds for every family is given to illustrate the corresponding range. The shifts for the carbons of interest are given in parentheses for each carbon as it appears either from left to right in the formula or by the underscore.<sup>1-14</sup>

### **REFERENCES**

1. Yoder, C.H. and Schaeffer, C.D., Jr., *Introduction to Multinuclear NMR: Theory and Application*, Benjamin/Cummings Publishing Co., Menlo Park, CA, 1987.
2. Brown, D.W., A short set of  $^{13}\text{C}$ -NMR correlation tables, *J. Chem. Ed.*, 62, 209, 1985.
3. Silverstein, R.M. and Webster, F.X., *Spectrometric Identification of Organic Compounds*, 6th ed., John Wiley & Sons, New York, 1998.
4. Becker, E.D., *High Resolution NMR, Theory and Chemical Applications*, 2nd ed., Academic Press, New York, 1980.
5. Gunther, H., *NMR Spectroscopy: Basic Principles, Concepts and Applications in Chemistry*, Wiley, New York, 2003.
6. Kitamaru, R., *Nuclear Magnetic Resonance: Principles and Theory*, Elsevier Science, Amsterdam, 1990.
7. Lambert, J.B., Holland, L.N., and Mazzola, E.P., *Nuclear Magnetic Resonance Spectroscopy: Introduction to Principles, Applications and Experimental Methods*, Prentice Hall, Englewood Cliffs, NJ, 2003.
8. Bovey, F.A. and Mirau, P.A., *Nuclear Magnetic Resonance Spectroscopy*, 2nd ed., Academic Press, New York, 1988.
9. Harris, R.K. and Mann, B.E., *NMR and the Periodic Table*, Academic Press, London, 1978.
10. Hore, P.J., *Nuclear Magnetic Resonance*, Oxford University Press, Oxford, 1995.
11. Nelson, J.H., *Nuclear Magnetic Resonance Spectroscopy*, 2nd ed., Wiley, New York, 2003.
12. Levy, G.C., Lichter, R.L., and Nelson, G.L., *Carbon-13 Nuclear Magnetic Resonance Spectroscopy*, 2nd ed., Wiley, New York, 1980.
13. Pihlaja, K. and Kleinpeter, E., *Carbon-13 NMR Chemical Shifts in Structural and Stereochemical Analysis*, VCH, New York, 1994.
14. *Aldrich Library of  $^1\text{H}$  and  $^{13}\text{C}$  FT-NMR Spectra*, Aldrich Chemical Company, Milwaukee, 1996.

<sup>13</sup>C NMR Absorptions of Major Functional Groups

δ (ppm)	Group	Family	Example (δ of Underlined Carbon)
220–165	>C=O	Ketones	(CH <sub>3</sub> ) <sub>2</sub> <u>C</u> O (206.0)
			(CH <sub>3</sub> ) <sub>2</sub> CH <u>C</u> OCH <sub>3</sub> (212.1)
		Aldehydes	CH <sub>3</sub> <u>C</u> HO (199.7)
		α,β-Unsaturated carbonyls	CH <sub>3</sub> CH=CH <u>C</u> HO (192.4)
			CH <sub>2</sub> =CH <u>C</u> OCH <sub>3</sub> (169.9)
		Carboxylic acids	H <u>C</u> O <sub>2</sub> H (166.0)
			CH <sub>3</sub> <u>C</u> O <sub>2</sub> H (178.1)
		Amides	H <u>C</u> ONH <sub>2</sub> (165.0)
			CH <sub>3</sub> <u>C</u> ONH <sub>2</sub> (172.7)
		Esters	CH <sub>3</sub> CO <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> (170.3)
140–120	>C=C<	Aromatic	CH <sub>2</sub> =CH <u>C</u> O <sub>2</sub> CH <sub>3</sub> (165.5)
			C <sub>6</sub> H <sub>6</sub> (128.5)
		Alkenes	CH <sub>2</sub> =CH <sub>2</sub> (123.2)
			CH <sub>2</sub> =CHCH <sub>3</sub> (115.9, 136.2)
			CH <sub>2</sub> =CHCH <sub>2</sub> Cl (117.5, 133.7)
125–115	–C≡N	Nitriles	CH <sub>3</sub> CH=CHCH <sub>2</sub> CH <sub>3</sub> (132.7)
80–70	–C≡C–	Alkynes	CH <sub>3</sub> – <u>C</u> ≡N (117.7)
70–45	→C–O	Esters	H <u>C</u> ≡CH (71.9)
			CH <sub>3</sub> <u>C</u> ≡CCH <sub>3</sub> (73.9)
		Alcohols	CH <sub>3</sub> OOCCH <sub>2</sub> CH <sub>3</sub> (57.6, 67.9)
40–20	→C–NH <sub>2</sub>	Amines	HOCH <sub>3</sub> (49.0)
			HOCH <sub>2</sub> CH <sub>3</sub> (57.0)
			CH <sub>3</sub> NH <sub>2</sub> (26.9)
30–15	–S–CH <sub>3</sub>	Sulfides (thioethers)	CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub> (35.9)
30–(–2.3)	>CH–	Alkanes, cycloalkanes	C <sub>6</sub> H <sub>5</sub> –S– <u>CH</u> <sub>3</sub> 15.6
			<u>CH</u> <sub>4</sub> (–2.3)
			<u>CH</u> <sub>3</sub> CH <sub>3</sub> (5.7)
			CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub> (15.8, 16.3)
			CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> (13.4, 25.2)
			CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> (13.9, 22.8, 34.7)
			Cyclohexane (26.9)

## **<sup>13</sup>C NMR CHEMICAL SHIFTS OF ORGANIC FAMILIES**

The following bibliography should give a good set of references for the various organic families. This collection is by no means complete and should be updated regularly.

### **REFERENCES**

#### **Adamantanes**

Maciel, G.E., Dorn, H.C., Greene, R.L., Kleschick, W.A., Peterson, M.R., Jr., and Wahl, G.H., Jr., <sup>13</sup>C chemical shifts of monosubstituted adamantanes, *Org. Magn. Reson.*, 6, 178, 1974.

#### **Amides**

Jones, R.G. and Wilkins, J.M., Carbon-13 NMR spectra of a series of parasubstituted *N,N*-dimethylbenzamides, *Org. Magn. Reson.*, 11, 20, 1978.

#### **Benzazoles**

Sohr, P., Manyai, G., Hideg, K., Hankovszky, H., and Lex, L., Benzazoles. XIII. Determination of the E and Z configuration of isomeric 2-(2-benzimidazolyl)-di- and tetra-hydrothiophenes by IR, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, *Org. Magn. Reson.*, 14, 125, 1980.

#### **Carbazoles**

Giraud, J. and Marzin, C., Comparative <sup>13</sup>C NMR study of deuterated and undeuterated dibenzothiophenes, dibenzofurans, carbazoles, fluorenes, and fluorenones, *Org. Magn. Reson.*, 12, 647, 1979.

#### **Chlorinated Compounds**

Hawkes, G.E., Smith, R.A., and Roberts, J.D., Nuclear magnetic resonance spectroscopy: carbon-13 chemical shifts of chlorinated organic compounds, *J. Org. Chem.*, 39, 1276, 1974.

Mark, V. and Weil, E.D., The isomerization and chlorination of decachlorobi-2,4-cyclopentadien-1-yl, *J. Org. Chem.*, 36, 676, 1971.

#### **Diazoles and Diazines**

Faure, R., Vincent, E.J., Assef, G., Kister, J., and Metzger, J., Carbon-13 NMR study of substituent effects in the 1,3-diazole and -diazine series, *Org. Magn. Reson.*, 9, 688, 1977.

#### **Disulfides**

Bass, S.W. and Evans, S.A., Jr., Carbon-13 nuclear magnetic resonance spectral properties of alkyl disulfides, thiosulfonates, and thiosulfonates, *J. Org. Chem.*, 45, 710, 1980.

Freeman, F. and Angeletakis, C.N., Carbon-13 nuclear magnetic resonance study of the conformations of disulfides and their oxide derivatives, *J. Org. Chem.*, 47, 4194, 1982.

Takata, T., Iida, K., and Oae, S., <sup>13</sup>C-NMR chemical shifts and coupling constants J<sub>C-H</sub> of six membered ring systems containing sulfur-sulfur linkage, *Heterocycles*, 15, 847, 1981.



## Fluorenes and Fluorenones

Giraud, J. and Marzin, C., Comparative  $^{13}\text{C}$  NMR study of deuterated and undeuterated dibenzothiophenes, dibenzofurans, carbazoles, fluorenes and fluorenones, *Org. Magn. Reson.*, 12, 647, 1979.

## Furans

Giraud, H. and Marzin, C., Comparative  $^{13}\text{C}$  NMR study of deuterated and undeuterated dibenzothiophenes, dibenzofurans, carbazoles, fluorenes and fluorenones, *Org. Magn. Reson.*, 12, 647, 1979.

## Imines

Allen, M. and Roberts, J.D., Effects of protonation and hydrogen bonding on carbon-13 chemical shifts of compounds containing the  $>\text{C}=\text{N}$ -group, *Can. J. Chem.*, 59, 451, 1981.

## Oxathianes

Murray, W.T., Kelly, J.W., and Evans, S.A., Jr., Synthesis of substituted 1,4-oxathianes, mechanistic details of diethoxytriphenylphosphorane — and triphenylphosphine/tetra-chloromethane — promoted cyclo-dehydrations and  $^{13}\text{C}$  NMR spectroscopy, *J. Org. Chem.*, 52, 525, 1987.

Szarek, W.A., Vyas, D.M., Sepulchre, A.M., Gero, S.D., and Lukacs, G., Carbon-13 nuclear magnetic resonance spectra of 1,4-oxathiane derivatives, *Can. J. Chem.*, 52, 2041, 1974.

## Oximes

Allen, M. and Roberts, J.D., Effects of protonation and hydrogen bonding on carbon-13 chemical shifts of compounds containing the  $>\text{C}=\text{N}$ -group, *Can. J. Chem.*, 59, 451, 1981.

## Polynuclear Aromatics (Naphthalenes, Anthracenes, Pyrenes)

Adcock, W., Aurangzeb, M., Kitching, W., Smith, N., and Doddzell, D., Substituent effects of carbon-13 nuclear magnetic resonance: concerning the  $\pi$ -inductive effect, *Aust. J. Chem.*, 27, 1817, 1974.

DuVernet, R. and Boekelheide, V., Nuclear magnetic resonance spectroscopy: ring-current effects on carbon-13 chemical shifts, *Proc. Natl. Acad. Sci. U.S.A.*, 71, 2961, 1974.

## Pyrazoles

Puar, M.S., Rovnyak, G.C., Cohen, A.I., Toeplitz, B., and Gougoutas, J.Z., Orientation of the sulfoxide bond as a stereochemical probe: synthesis and  $^1\text{H}$  and  $^{13}\text{C}$  NMR of substituted thiopyrano[4,3-c]pyrazoles, *J. Org. Chem.*, 44, 2513, 1979.

## Sulfides

Chauhan, M.S., and Still, I.W.J.,  $^{13}\text{C}$  nuclear magnetic resonance spectra of organic sulfur compounds: cyclic sulfides, sulfoxides, sulfones, and thiones, *Can. J. Chem.*, 53, 2880, 1975.

Gokel, G.W., Gerdes, H.M., and Dishong, D.M., Sulfur heterocycles. 3. Heterogenous, phase-transfer, and acid catalyzed potassium permanganate oxidation of sulfides to sulfones and a survey of their carbon-13 nuclear magnetic resonance spectra, *J. Org. Chem.*, 45, 3634, 1980.

Mohraz, M., Jiam-qi, W., Heilbronner, E., Solladie-Cavallo, A., and Matloubi-Moghadam, F., Some comments on the conformation of methyl phenyl sulfides, sulfoxides, and sulfones, *Helv. Chim. Acta*, 64, 97, 1981.

Srinivasan, C., Perumal, S., Arumugam, N., and Murugan, R., Linear free-energy relationship in naphthalene system-substituent effects on carbon-13 chemical shifts of substituted naphthylmethyl sulfides, *Ind. J. Chem.*, 25A, 227, 1986.

## Sulfites

Buchanan, G.W., Cousineau, C.M.E., and Mundell, T.C., Trimethylene sulfite conformations: effects of sterically demanding substituents at C-4,6 on ring geometry as assessed by  $^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic resonance, *Can. J. Chem.*, 56, 2019, 1978.

## Sulfonamides

Chang, C., Floss, H.G., and Peck, G.E., Carbon-13 magnetic resonance spectroscopy of drugs: sulfonamides, *J. Med. Chem.*, 18, 505, 1975.

## Sulfones (See Also Other Families for the Corresponding Sulfones)

Balaji, T. and Reddy, D.B., Carbon-13 nuclear magnetic resonance spectra of some new arylcyclopropyl sulphones, *Ind. J. Chem.*, 18B, 454, 1979.

Fawcett, A.H., Ivin, K.J., and Stewart, C.D., Carbon-13 NMR spectra of monosulphones and disulphones: substitution rules and conformational effects, *Org. Magn. Reson.*, 11, 360, 1978.

Gokel, G.W., Gerdes, H.M., and Dishong, D.M., Sulfur heterocycles. 3. Heterogeneous, phase-transfer, and acid catalyzed potassium permanganate oxidation of sulfides to sulfones and a survey of their carbon-13 nuclear magnetic resonance spectra, *J. Org. Chem.*, 45, 3634, 1980.

## Sulfoxides (See Also Other Families for the Corresponding Sulfoxides)

Gatti, G., Levi, A., Lucchini, V., Modena, G., and Scorrano, G., Site of protonation in sulfoxides: carbon-13 nuclear magnetic resonance evidence, *J. Chem. Soc. Chem. Commun.*, 251, 1973.

Harrison, C.R. and Hodge, P., Determination of the configuration of some penicillin S-oxides by  $^{13}\text{C}$  nuclear magnetic resonance spectroscopy, *J. Chem. Soc. Perkin Trans.*, I, 1772, 1976.

## Sulfur Ylides

Matsuyama, H., Minato, H., and Kobayashi, M., Electrophilic sulfides (II) as a novel catalyst. V. Structure, nucleophilicity, and steric compression of stabilized sulfur ylides as observed by  $^{13}\text{C}$ -NMR spectroscopy, *Bull. Chem. Soc. Jpn.*, 50, 3393, 1977.

## Thianes

Barbarella, G., Dembech, P., Garbesi, A., and Fara, A.,  $^{13}\text{C}$  NMR of organosulfur compounds. II.  $^{13}\text{C}$  chemical shifts and conformational analysis of methyl substituted thiacyclohexanes, *Org. Magn. Reson.*, 8, 469, 1976.

Block, E., Bazzi, A.A., Lambert, J.B., Wharry, S.M., Andersen, K.K., Dittmer, D.C., Patwardhan, B.H., and Smith, J.H., Carbon-13 and oxygen-17 nuclear magnetic resonance studies of organosulfur compounds: the four-membered-ring-sulfone effect, *J. Org. Chem.*, 45, 4807, 1980.

Murray, W.T., Kelly, J.W., and Evans, S.A., Jr., Synthesis of substituted 1,4-oxathianes: mechanistic details of diethoxytriphenyl phosphorane and triphenylphosphine/tetrachloromethane — promoted cyclodehydrations and  $^{13}\text{C}$  NMR spectroscopy, *J. Org. Chem.*, 52, 525, 1987.

Rooney, R.P., and Evans, S.A., Jr., Carbon-13 nuclear magnetic resonance spectra of trans-1-thiadecalin, trans-1,4-dithiadecalin, trans-1,4-oxathiadecalin, and the corresponding sulfoxides and sulfones, *J. Org. Chem.*, 45, 180, 1980.

Willer, R.L. and Eliel, E.L., Conformational analysis. 34. Carbon-13 nuclear magnetic resonance spectra of saturated heterocycles. 6. Methylthianes, *J. Am. Chem. Soc.*, 99, 1925, 1977.

## Thiazines

Fronza, G., Mondelli, R., Scapini, G., Ronsisvalle, G., and Vittorio, F.,  $^{13}\text{C}$  NMR of N-heterocycles: conformation of phenothiazines and 2,3-diazaphenothiazines, *J. Magn. Reson.*, 23, 437, 1976.

## Thiazoles

Chang, G., Floss, H.G., and Peck, G.E., Carbon-13 magnetic resonance spectroscopy of drugs: sulfonamides, *J. Med. Chem.*, 18, 505, 1975.

Elguero, J., Faure, R., Lazaro, R., and Vincent, E.J.,  $^{13}\text{C}$  NMR study of benzothiazole and its nitroderivatives, *Bull. Soc. Chim. Belg.*, 86, 95, 1977.

Faure, R., Galy, J.P., Vincent, E.J., and Elguero, J., Study of polyheteroaromatic pentagonal heterocycles by carbon-13 NMR: thiazoles and thiazolo[2,3-e]tetrazoles, *Can. J. Chem.*, 56, 46, 1978.

Harrison, C.R. and Hodge, P., Determination of the configuration of some penicillin S-oxides by  $^{13}\text{C}$  nuclear magnetic resonance spectroscopy, *J. Chem. Soc. Perkin Trans.*, 1, 1772, 1976.

## Thiochromanones

Chauhan, M.S. and Still, I.W.J.,  $^{13}\text{C}$  nuclear magnetic resonance spectra of organic sulfur compounds: cyclic sulfides, sulfoxides, sulfones and thiones, *Can. J. Chem.*, 53, 2880, 1975.

## Thiones

Chauhan, M.S. and Still, I.W.J.,  $^{13}\text{C}$  nuclear magnetic resonance spectra of organic sulfur compounds: cyclic sulfides, sulfoxides, sulfones and thiones, *Can. J. Chem.*, 53, 2880, 1975.

## Thiophenes

Balkau, F., Fuller, M.W., and Heffernan, M.L., Deceptive simplicity in ABMX N.M.R. spectra. I. Dibenzothiophen and 9,9'-dicarbazyl, *Aust. J. Chem.*, 24, 2293, 1971.

Benassi, R., Folli, U., Iarossi, D., Schenetti, L., and Tadei, F., Conformational analysis of organic carbonyl compounds. Part 3. A  $^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic resonance study of formyl and acetyl derivatives of benzo[b]thiophen, *J. Chem. Soc. Perkin Trans.*, II, 911, 1983.

Clark, P.D., Ewing, D.F., and Scrowston, R.M., NMR studies of sulfur heterocycles: III.  $^{13}\text{C}$  spectra of benzo[b]thiophene and the methylbenzo[b]thiophenes, *Org. Magn. Reson.*, 8, 252, 1976.

Fujieda, K., Takahashi, K., and Sone, T., The C-13 NMR spectra of thiophenes. II. 2-Substituted thiophenes, *Bull. Chem. Soc. Jpn.*, 58, 1587, 1985.

Geneste, P., Olive, J.L., Ung, S.N., El Faghi, M.E.A., Easton, J.W., Beierbeck, H., and Saunders, J.K., Carbon-13 nuclear magnetic resonance study of benzo[b]thiophenes and benzo[b]thiophene S-oxides and S,S-dioxides, *J. Org. Chem.*, 44, 2887, 1979.

Giraud, J. and Marzin, C., Comparative  $^{13}\text{C}$  NMR study of deuterated and undeuterated dibenzothiophenes, dibenzofurans, carbazoles, fluorenes and fluorenones, *Org. Magn. Reson.*, 12, 647, 1979.

Kiezel, L., Liszka, M., and Rutkowski, M., Carbon-13 magnetic resonance spectra of benzothiophene and dibenzothiophene, *Spec. Lett.*, 12, 45, 1979.

Osamura, Y., Sayanagi, O., and Nishimoto, K., C-13 NMR chemical shifts and charge densities of substituted thiophenes: the effect of vacant  $d\pi$  orbitals, *Bull. Chem. Soc. Jpn.*, 49, 845, 1976.

Perjessy, A., Janda, M., and Boykin, D.W., Transmission of substituent effects in thiophenes: infrared and carbon-13 nuclear magnetic resonance studies, *J. Org. Chem.*, 45, 1366, 1980.

Satonaka, H. and Watanabe, M., NMR spectra of 2-(2-nitrovinyl) thiophenes, *Bull. Chem. Soc. Jpn.*, 58, 3651, 1985.

Stuart, J.G., Quast, M.J., Martin, G.E., Lynch, V.M., Simonsen, H., Lee, M.L., Castle, R.N., Dallas, J.L., John B.K., and Johnson, L.R.F., Benzannelated analogs of phenanthro [1,2-b]-[2,1-b]thiophene: synthesis and structural characterization by two-dimensional NMR and x-ray techniques, *J. Heterocyclic Chem.*, 23, 1215, 1986.

## Thiopyrans

Senda, Y., Kasahara, A., Izumi, T., and Takeda, T., Carbon-13 NMR spectra of 4-chromanone, 4H-1-benzothiopyran-4-one, 4H-1-benzothiopyran-4-one 1,1-dioxide, and their substituted homologs, *Bull. Chem. Soc. Jpn.*, 50, 2789, 1977.

## Thiosulfinates and Thiosulfonates

Bass, S.W. and Evans, S.A., Jr., Carbon-13 nuclear magnetic resonance spectral properties of alkyl disulfides, thiosulfinates, and thiosulfonates, *J. Org. Chem.*, 45, 710, 1980.

## **<sup>15</sup>N CHEMICAL SHIFTS FOR COMMON STANDARDS**

The following table lists the <sup>15</sup>N chemical shifts (in ppm) for common standards. The estimated precision is better than 0.1 ppm. Nitromethane, according to Levy and Lichter,<sup>1</sup> is the most suitable primary measurement reference, but has the disadvantage of lying in the low-field end of the spectrum. Thus, ammonia (which lies in the most upfield region) is the most suitable for routine experimental use.<sup>1-6</sup>

### **REFERENCES**

1. Levy, G.C. and Lichter, R.L., *Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy*, John Wiley & Sons, New York, 1979.
2. Lambert, J.B., Shurvell, H.F., Verbit, L., Cooks, R.G., and Stout, G.H., *Organic Structural Analysis*, MacMillan, New York, 1976.
3. Witanowski, M., Stefaniak, L., Szymanski, S., and Januszewski, H., External neat nitromethane scale for nitrogen chemical shifts, *J. Magn. Reson.*, 28, 217, 1977.
4. Srinivasan, P.R. and Lichter, R.L., Nitrogen-15 nuclear magnetic resonance spectroscopy: evaluation of chemical shift references, *J. Magn. Reson.*, 28, 227, 1977.
5. Briggs, J.M. and Randall, E.W., Nitrogen-15 chemical shifts in concentrated aqueous solutions of ammonium salts, *Mol. Phys.*, 26, 699, 1973.
6. Becker, E.D., Proposed scale for nitrogen chemical shifts, *J. Magn. Reson.*, 4, 142, 1971.

**<sup>15</sup>N Chemical Shifts for Common Standards**

Compound	Formula	Conditions	Chemical Shift (ppm)
Ammonia	NH <sub>3</sub>	Vapor (0.5 MPa)	-15.9
		Liquid (25°C), anhydrous	0.0
		Liquid (-50°C)	3.37
Ammonium nitrate	NH <sub>4</sub> NO <sub>3</sub>	Aqueous HNO <sub>3</sub>	21.60
		Aqueous solution (saturated)	20.68
Ammonium chloride	NH <sub>4</sub> Cl	2.9 M (in 1 M HCl)	24.93
		1.0 M (in 10 M HCl)	30.31
		Aqueous solution (saturated)	27.34
Tetraethylammonium chloride	(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> N <sup>+</sup> Cl <sup>-</sup>	Aqueous solution (saturated)	43.54
		Chloroform solution (saturated)	45.68
		Aqueous solution (0.3 M)	63.94
		Aqueous solution (saturated)	64.39
		Chloroform solution (0.075 M)	65.69
Tetramethyl urea	[(CH <sub>3</sub> ) <sub>2</sub> N] <sub>2</sub> CO	Neat	62.50
Dimethylformamide (DMF)	(CH <sub>3</sub> ) <sub>2</sub> NCHO	Neat	103.81
Nitric acid (aqueous solution)	HNO <sub>3</sub>	1 M	375.80
		2 M	367.84
		9 M	365.86
		10 M	362.00
		15.7 M	348.92
Sodium nitrate	NaNO <sub>3</sub>	Aqueous solution (saturated)	376.53
Ammonium nitrate	NH <sub>4</sub> NO <sub>3</sub>	Aqueous solution (saturated)	376.25
		5 M (in 2 M HNO <sub>3</sub> )	375.59
		4 M (in 2 M HNO <sub>3</sub> )	374.68
Nitromethane	CH <sub>3</sub> NO <sub>2</sub>	1:1 (v/v) in CDCl <sub>3</sub>	379.60
		0.03 M Cr(acac) <sub>3</sub>	380.23
		Neat	

## <sup>15</sup>N CHEMICAL SHIFTS OF MAJOR CHEMICAL FAMILIES

The following table contains <sup>15</sup>N chemical shifts of various organic nitrogen compounds. Chemical shifts are expressed relative to different standards (NH<sub>3</sub>, NH<sub>4</sub>Cl, CH<sub>3</sub>NO<sub>2</sub>, NH<sub>4</sub>NO<sub>3</sub>, HNO<sub>3</sub>, etc.) and are interconvertible. Chemical shifts are sensitive to hydrogen bonding and are solvent dependent, as seen in the case of pyridine (see table footnote b below). Consequently, the reference as well as the solvent should always accompany chemical shift data. No data are given on peptides and other biochemical compounds. All shifts are relative to ammonia unless otherwise specified. A section of miscellaneous data gives the chemical shift of special compounds relative to unusual standards.<sup>1-15</sup>

### REFERENCES

1. Levy, G.C. and Lichter, R.L., *Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy*, John Wiley & Sons, New York, 1979.
2. Yoder, C.H. and Schaeffer, C.D., Jr., *Introduction to Multinuclear NMR*, Benjamin/Cummings, Menlo Park, CA, 1987.
3. Duthaler, R.O. and Roberts, J.D., Effects of solvent, protonation, and N-alkylation on the <sup>15</sup>N chemical shifts of pyridine and related compounds, *J. Am. Chem. Soc.*, 100, 4969, 1978.
4. Duthaler, R.O. and Roberts, J.D., Steric and electronic effects on <sup>15</sup>N chemical shifts of saturated aliphatic amines and their hydrochlorides, *J. Am. Chem. Soc.*, 100, 3889, 1978.
5. Kozerski, L. and von Philipsborn, W., <sup>15</sup>N chemical shifts as a conformational probe in enamines: a variable temperature study at natural isotope abundance, *Org. Magn. Reson.*, 17, 306, 1981.
6. Duthaler, R.O. and Roberts, J.D., Steric and electronic effects on <sup>15</sup>N chemical shifts of piperidine and decahydroquinoline hydrochlorides, *J. Am. Chem. Soc.*, 100, 3882, 1978.
7. Duthaler, R.O. and Roberts, J.D., Nitrogen-15 nuclear magnetic resonance spectroscopy: solvent effects on the <sup>15</sup>N chemical shifts of saturated amines and their hydrochlorides, *J. Magn. Reson.*, 34, 129, 1979.
8. Psota, L., Franzen-Sieveling, M., Turnier, J., and Lichter, R.L., Nitrogen nuclear magnetic resonance spectroscopy: nitrogen-15 and proton chemical shifts of methylanilines and methylanilinium ions, *Org. Magn. Reson.*, 11, 401, 1978.
9. Subramanian, P.K., Chandra Sekara, N., and Ramalingam, K., Steric effects on nitrogen-15 chemical shifts of 4-aminooxanes (tetrahydropyrans), 4-amino-thianes, and the corresponding N,N-dimethyl derivatives: use of nitrogen-15 shifts as an aid in stereochemical analysis of these heterocyclic systems, *J. Org. Chem.*, 47, 1933, 1982.
10. Schuster, I.I. and Roberts, J.D., Proximity effects on nitrogen-15 chemical shifts of 8-substituted 1-nitronaphthalenes and 1-naphthylamines, *J. Org. Chem.*, 45, 284, 1980.
11. Kupce, E., Liepins, E., Pudova, O., and Lukevics, E., Indirect nuclear spin-spin coupling constants of nitrogen-15 to silicon-29 in silylamines, *J. Chem. Soc. Chem. Commun.*, 581, 1984.
12. Allen, M. and Roberts, J.D., Effects of protonation and hydrogen bonding on nitrogen-15 chemical shifts of compounds containing the >C=N-group, *J. Org. Chem.*, 45, 130, 1980.
13. Brownlee, R.T.C. and Sadek, M., Natural abundance <sup>15</sup>N chemical shifts in substituted benzamides and thiobenzamides, *Magn. Reson. Chem.*, 24, 821, 1986.
14. Dega-Szafran, Z., Szafran, M., Stefaniak, L., Brevard, C., and Bourdonneau, M., Nitrogen-15 nuclear magnetic resonance studies of hydrogen bonding and proton transfer in some pyridine trifluoroacetates in dichloromethane, *Magn. Reson. Chem.*, 24, 424, 1986.
15. Lambert, J.B., Shurvell, H.F., Verbit, L., Cooks, R.G., and Stout, G.H., *Organic Structural Analysis*, Macmillan, New York, 1976.

**<sup>15</sup>N Chemical Shifts of Major Chemical Families**

Chemical Shift Range (ppm)	Family	Example (δ)
<930	Nitroso compounds	C <sub>6</sub> H <sub>5</sub> -NO (913, 930)
608	Sodium nitrite	NaNO <sub>2</sub>
~500	Azo compounds	C <sub>6</sub> H <sub>5</sub> -N=N-C <sub>6</sub> H <sub>5</sub> (510)
380–350	Nitro compounds	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> (370.3); CH <sub>3</sub> NO <sub>2</sub> (380.2); 4-F-C <sub>6</sub> H <sub>4</sub> -NO <sub>2</sub> (368.5); 1,3-(NO <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>4</sub> (365.4)
367	Nitric acid (8.57 M)	HNO <sub>3</sub>
360–325	Nitramines	CH <sub>3</sub> NHNO <sub>2</sub> (355.6); CH <sub>3</sub> O <sub>2</sub> CNHNNO <sub>2</sub> (334.9)
350–300	Pyridines	C <sub>5</sub> H <sub>5</sub> N (317) <sup>b</sup> (gas); 4-CH <sub>3</sub> -C <sub>5</sub> H <sub>4</sub> N (309.3); 4-NH <sub>2</sub> -C <sub>5</sub> H <sub>4</sub> N (271.5); 4-NC-C <sub>5</sub> H <sub>4</sub> N (327.9)
~310	Imines (aromatic)	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C=NH (308); C <sub>6</sub> H <sub>5</sub> CH=NCH <sub>3</sub> (318); C <sub>6</sub> H <sub>5</sub> CH=NC <sub>6</sub> H <sub>5</sub> (326)
310.1	Nitrogen (gas)	N <sub>2</sub>
250–200	Pyridinium salts	C <sub>5</sub> H <sub>5</sub> NH <sup>+</sup> (215)
260–175	Cyanides (nitriles)	CH <sub>3</sub> CN (239.5, 245); C <sub>6</sub> H <sub>5</sub> CN (258.7); KCN 177.8
~160	Pyrroles	C <sub>4</sub> H <sub>4</sub> NH (158)
	Isonitriles	CH <sub>3</sub> NC (162)
~150	Thioamides	CH <sub>3</sub> C(=S)NH <sub>2</sub> (150.2)
120–110	Lactams	HN(CH <sub>2</sub> ) <sub>3</sub> C=O (five-membered ring; 114.7) HN(CH <sub>2</sub> ) <sub>6</sub> C=O (eight-membered ring; 117.7)
110–100	Amides	C <sub>6</sub> H <sub>5</sub> CONH <sub>2</sub> (100); CH <sub>3</sub> CONH <sub>2</sub> (103.4); CH <sub>3</sub> CONHCH <sub>3</sub> (105.8); CH <sub>3</sub> CON(CH <sub>3</sub> ) <sub>2</sub> (103.8); HCONH <sub>2</sub> (108.5)
125–90	Sulfonamides	CH <sub>3</sub> SO <sub>2</sub> NH <sub>2</sub> (95); C <sub>6</sub> H <sub>5</sub> SO <sub>2</sub> NH <sub>2</sub> (94.3)
~100	Hydrazines	C <sub>6</sub> H <sub>5</sub> NHNHC <sub>6</sub> H <sub>5</sub> (96)
110–60	Ureas	[H <sub>2</sub> N] <sub>2</sub> CO (75, 82); [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>2</sub> CO (63.5); [C <sub>6</sub> H <sub>5</sub> NH] <sub>2</sub> CO (107.7)
100–70	Aminophosphines	C <sub>6</sub> H <sub>5</sub> NHP(CH <sub>3</sub> ) <sub>2</sub> (71.1)
	Aminophosphine oxides	C <sub>6</sub> H <sub>5</sub> NHPO(CH <sub>3</sub> ) <sub>2</sub> (86.6)
70–50	Aromatic amines	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub> (55, 59) (–322.3) <sup>c</sup> ; C <sub>6</sub> H <sub>5</sub> NH <sub>3</sub> <sup>+</sup> (48) (–326.4) <sup>c</sup> , 26.1 <sup>g</sup> ; <i>p</i> -O <sub>2</sub> N-C <sub>6</sub> H <sub>4</sub> -NH <sub>2</sub> (70)
40–0	Aliphatic amines	CH <sub>3</sub> NH <sub>2</sub> (1.3) <sup>a</sup> (–371) <sup>c</sup> ; (CH <sub>3</sub> ) <sub>2</sub> NH (–363.3) <sup>c</sup> (–364.9) <sup>d</sup> , 6.7 <sup>a</sup> ; (CH <sub>3</sub> ) <sub>3</sub> N (–356.9) <sup>c</sup> (–360.7) <sup>d</sup> , 13.0 <sup>a</sup>
50–10	Isonitriles	CH <sub>3</sub> NCO (14.1); C <sub>6</sub> H <sub>5</sub> NCO (46.5)
65–20	Ammonium salts	NH <sub>4</sub> Cl (26.1) <sup>a</sup> ; CH <sub>3</sub> NH <sub>3</sub> Cl (24.5); (CH <sub>3</sub> ) <sub>2</sub> NH <sub>2</sub> Cl (26.6); (CH <sub>3</sub> ) <sub>3</sub> NHCl (33.8); (CH <sub>3</sub> ) <sub>4</sub> NCl (44.7)
~15	Isocyanates	CH <sub>3</sub> NCO (14.1)

**<sup>15</sup>N Chemical Shifts of Major Chemical Families (continued)**

Chemical Shift Range (ppm)	Family	Example (δ)
<b>Miscellaneous</b>		
–130 to –110 and ~212	Imidazoles	<i>N</i> -Methylimidazole (–111.4, pyridine N; –215.7, pyrrole N) <sup>c</sup>
–345 to –310 <sup>c</sup>	Piperidine, hydrochloride salts	Piperidinium hydrochloride (–344.8); 2-methyl piperidinium hydrochloride (–322.1) <sup>d</sup>
	Decahydroquinolines, hydrochloride salts	<i>trans</i> -Decahydroquinolinium hydrochloride (–322.5); <i>cis</i> -decahydroquinolinium hydrochloride (–328.5)
–293 to –280 <sup>e</sup>	Enaminones	CH <sub>3</sub> C(=O)CH=CHNHCH <sub>3</sub> [(E)-(–294.2); (Z)-(–285.9)]
35–15 <sup>f</sup>	4-Aminotetrahydropyrans	2,6-Diphenyl 4-aminotetrahydropyran (34.5)
	4-Aminotetrahydrothiopyrans	2,6-Diphenyl 4-aminotetrahydrothiopyran (33.6)
–325 to –310 <sup>g</sup>	1-Naphthylamines	8-Nitro-1-naphthylamine (313.9)
–350 to –300 <sup>h</sup>	Silylamines	HN[Si(CH <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub> (–354.2)

<sup>a</sup> Downfield from anhydrous liquid ammonia, ±0.2 ppm unless otherwise specified.<sup>1</sup> (The indicated superscript numbers refer to the reference list at the beginning of this table.)

<sup>b</sup> Varies with solvent, for instance, cyclohexane (315.5), benzene (312.1), chloroform (304.5), methanol (292.1), water (289), 2,2,2-trifluoroethanol (277.1). All chemical shifts relative to ammonia.<sup>2</sup>

<sup>c</sup> Upfield from external HNO<sub>3</sub> (1 *M*) (CH<sub>3</sub>OH).<sup>4,6,7</sup>

<sup>d</sup> Upfield from external HNO<sub>3</sub> (1 *M*) (cyclohexane).<sup>6,7</sup>

<sup>e</sup> Relative to external CH<sub>3</sub><sup>15</sup>NO<sub>2</sub>.<sup>5</sup>

<sup>f</sup> With respect to an external standard of 5 *M* <sup>15</sup>NH<sub>4</sub>NO<sub>3</sub> in 2 *M* HNO<sub>3</sub> (<sup>15</sup>NH<sub>4</sub>NO<sub>3</sub> = 21.6 ppm relative to anhydrous ammonia).<sup>9</sup>

<sup>g</sup> In ppm upfield from external 1 *M* D<sup>15</sup>NO<sub>3</sub> in D<sub>2</sub>O (DMSO).<sup>10</sup>

<sup>h</sup> Relative to N(SiH<sub>3</sub>) (50% in CDCl<sub>3</sub>).<sup>11</sup>



## SPIN-SPIN COUPLING TO $^{15}\text{N}$

The following list gives representative spin-spin coupling ranges ( $J_{\text{NH}}$  in Hz) to  $^{15}\text{N}$ .<sup>1-9</sup>

### REFERENCES

1. Levy, G.C. and Lichter, R.L., *Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy*, John Wiley & Sons, New York, 1979.
2. DelBene, J.E. and Bartlett, R.J., N-N spin-spin coupling constants [ $2hJ(15\text{N}-15\text{N})$ ] across N-H: N hydrogen bonds in neutral complexes: to what extent does the bonding at the nitrogens influence  $2hJ\text{N}-\text{N}$ ? communication, *J. Am. Chem. Soc.*, 122, 10480 2000.
3. Del Bene, J.E., Perera, S.A., Bartlett, R.J., Yáñez, M., Mó, O., Elguero, J., and Alkorta, I., Two bond  $^{19}\text{F}-^{14}\text{N}$  spin spin coupling constants ( $^2hJ_{\text{F-N}}$ ) across F-H...H hydrogen bonds, *J. Phys. Chem.*, 107, 3121, 2003.
4. Duthaler, R.O. and Roberts, J.D., Effects of solvent, protonation, and N-alkylation on the  $^{15}\text{N}$  chemical shifts of pyridine and related compounds, *J. Am. Chem. Soc.*, 100, 4969, 1978.
5. Duthaler, R.O. and Roberts, J.D., Steric and electronic effects on  $^{15}\text{N}$  chemical shifts of saturated aliphatic amines and their hydrochlorides, *J. Am. Chem. Soc.*, 100, 3889, 1978.
6. Kozerski, L. and von Philipsborn, W.,  $^{15}\text{N}$  chemical shifts as a conformational probe in enamines: a variable temperature study at natural isotope abundance, *Org. Magn. Reson.*, 17, 306, 1981.
7. Subramanian, P.K., Chandra Sekara, N., and Ramalingam, K., Steric effects on nitrogen-15 chemical shifts of 4-aminooxanes (tetrahydropyrans), 4-amino-thianes, and the corresponding N,N-dimethyl derivatives: use of nitrogen-15 shifts as an aid in stereochemical analysis of these heterocyclic systems, *J. Org. Chem.*, 47, 1933, 1982.
8. Kupce, E., Liepins, E., Pudova, O., and Lukevics, E., Indirect nuclear spin-spin coupling constants of nitrogen-15 to silicon-29 in silylamines, *J. Chem. Soc. Chem. Commun.*, 581, 1984.
9. Axenrod, T., Structural effects on the one-bond  $15\text{N}-\text{H}$  coupling constant, in *NMR Spectroscopy of Nuclei Other Than Protons*, Axenrod, T. and Webb, G.A., Eds., Wiley Interscience, New York, 1974.

**<sup>15</sup>N–H Coupling Constants**

Bond Type	Family	J <sub>NH</sub>	Example
One bond	Ammonia	–61.2	NH <sub>3</sub>
	Amines, aliphatic (1°, 2°)	~ –65	CH <sub>3</sub> NH <sub>2</sub> (–64.5) (CH <sub>3</sub> ) <sub>2</sub> NH (–67.0)
	Ammonium salts	~ –75	CH <sub>3</sub> NH <sub>3</sub> Cl (–75.4) (CH <sub>3</sub> ) <sub>2</sub> NH <sub>2</sub> Cl (–76.1) C <sub>6</sub> H <sub>5</sub> NH <sub>3</sub> <sup>+</sup> (–76)
	Amines, aromatic (1°, 2°)	–78 to –95	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub> (–78.5) <i>p</i> -CH <sub>3</sub> O–C <sub>6</sub> H <sub>4</sub> –NH <sub>2</sub> (–79.4) <i>p</i> -O <sub>2</sub> N–C <sub>6</sub> H <sub>4</sub> –NH <sub>2</sub> (–92.6)
	Sulfonamides	~ –80	C <sub>6</sub> H <sub>5</sub> SO <sub>2</sub> NH <sub>2</sub> (–80.8)
	Hydrazines	–90 to –100	C <sub>6</sub> H <sub>5</sub> NHNH <sub>2</sub> (–89.6)
	Amides (1°, 2°)	–85 to –95	HCONH <sub>2</sub> (–88) (syn); (–92) (anti)
	Pyrroles	–95 to –100	Pyrrole (–96.53)
	Nitriles, salts	~ –135	CH <sub>3</sub> C≡NH <sup>+</sup> (–136)
Two bond	Amines	~ –1	CH <sub>3</sub> NH <sub>2</sub> (–1.0) (CH <sub>3</sub> ) <sub>3</sub> N (–0.85)
	Pyridinium salts	~ –3	C <sub>5</sub> H <sub>5</sub> NH <sup>+</sup> (–3)
	Pyrroles	~ –5	C <sub>4</sub> H <sub>4</sub> NH (–4.52)
	Thiazoles	~ –10	C <sub>3</sub> H <sub>3</sub> NS
	Pyridines	~ –10	C <sub>5</sub> H <sub>5</sub> N (–10.76)
	Oximes, syn	~ –15	>C=N–OH (syn)
	Oximes, anti	–2.5 to +2.5	>C=N–OH (anti)
Three bond	Nitriles, salts	~2 to 4	CH <sub>3</sub> C≡NH <sup>+</sup> (2.8)
	Amides	~1 to 2	CH <sub>3</sub> CONH <sub>2</sub> (1.3)
	Anilines	~1 to 2	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub> (1.5, 1.8)
	Pyridines	~0 to 1	C <sub>5</sub> H <sub>5</sub> N (0.2)
	Nitriles	–1 to –2	CH <sub>3</sub> C≡N (–1.7)
	Pyridinium salts	~ –4	C <sub>5</sub> H <sub>5</sub> NH <sup>+</sup> (–3.98)
	Pyrroles	~ –5	C <sub>4</sub> H <sub>4</sub> NH (–5.39)

**<sup>15</sup>N–<sup>13</sup>C Coupling Constants**

Bond Type	Family	J <sub>CH</sub> , H <sub>2</sub>	Example
One bond	Amines, aliphatic	~ –4	CH <sub>3</sub> NH <sub>2</sub> (–4.5) CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> NH <sub>2</sub> (–3.9)
	Ammonium salts, aliphatic	~ –5	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> NH <sub>3</sub> <sup>+</sup> (–4.4)
	Ammonium salts, aromatic	~ –9	C <sub>6</sub> H <sub>5</sub> NH <sub>3</sub> <sup>+</sup> (–8.9)
	Pyrroles	~ –10	C <sub>4</sub> H <sub>4</sub> NH (–10.3)
	Amines, aromatic	–11 to –15	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub> (–11.43)
	Nitro compounds	–10 to –15	CH <sub>3</sub> NO <sub>2</sub> (–10.5)
			C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> (–14.5)
	Nitriles	~ –17	CH <sub>3</sub> C≡N (–17.5)
	Amides	~ –14	C <sub>6</sub> H <sub>5</sub> NHCOCH <sub>3</sub> (–14.3) (CO); (–14.1) (C <sub>1</sub> )
Two bond	Amides	7–9	CH <sub>3</sub> CONH <sub>2</sub> (9.5)
	Nitriles	~3	CH <sub>3</sub> C≡N (3.0)
	Pyridines and N-derivatives	~1–3	C <sub>5</sub> H <sub>5</sub> N (2.53)
			C <sub>5</sub> H <sub>5</sub> NH <sup>+</sup> (2.01)
			C <sub>5</sub> H <sub>5</sub> NO (1.43)
	Amines, aliphatic	~1–2	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> (1.2)
	Nitro compounds, aromatic	~ –1 to –2	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> (–1.67)
	Amines, aromatic	~ –1 to –2	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub> (–2.68)
			C <sub>6</sub> H <sub>5</sub> NH <sub>3</sub> <sup>+</sup> (–1.5)
	Pyrroles	~ –4	C <sub>4</sub> H <sub>4</sub> NH (–3.92)
Three bond	Amides	9	CH <sub>2</sub> =CHCONH <sub>2</sub> (19)
	Ammonium salts	1–9	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> NH <sub>3</sub> <sup>+</sup> (1.3)
			C <sub>6</sub> H <sub>5</sub> NH <sub>3</sub> <sup>+</sup> (2.1)
	Pyridines	~3	C <sub>5</sub> H <sub>5</sub> N (2.53)
	Amines, aliphatic	1–3	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> NH <sub>2</sub> (1.4)
	Amines, aromatic	~ –1 to –3	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub> (–2.68)
	Nitro compounds	~ –2	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> (–1.67)
	Pyrroles	~ –4	C <sub>4</sub> H <sub>4</sub> NH (–3.92)

**<sup>15</sup>N–<sup>15</sup>N Coupling Constants**

Bond Type	Family	J <sub>NN</sub> , H <sub>2</sub>	Example
	Azocompounds	12–25	C <sub>6</sub> H <sub>5</sub> N=NC(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (17) (anti); (21) (syn)
	N-Nitrosamines	~19	(C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> ) <sub>2</sub> N–N=O (19)
	Hydrazones	~10	<i>p</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CH=N–NHC <sub>6</sub> H <sub>5</sub> (10.7)
	Hydrazines	~7	C <sub>6</sub> H <sub>5</sub> NHNH <sub>2</sub> (6.7)

**<sup>15</sup>N–<sup>19</sup>F Coupling Constants**

Bond Type	Family	J <sub>NF</sub> , H <sub>2</sub>	Example
	Difluorodiazines	~190 ( <sup>1</sup> J <sub>NF</sub> )	F–N=N–F (190)
		~102 ( <sup>2</sup> J <sub>NF</sub> )	F–N=N–F (102)
		~203 ( <sup>1</sup> J <sub>NF</sub> )	F–N=N–F (203)
		~52 ( <sup>2</sup> J <sub>NF</sub> )	F–N=N–F (52)
	Fluoropyridines		
	2-fluoro-	–52.5	
	3-fluoro-	+3.6	
	Fluoroanilines		
	2-fluoro-	0	1,2-C <sub>6</sub> H <sub>4</sub> F (NH <sub>2</sub> )
	3-fluoro-	0	1,3-C <sub>6</sub> H <sub>4</sub> F (NH <sub>2</sub> )
	4-fluoro-	1.5	1,4-C <sub>6</sub> H <sub>4</sub> F (NH <sub>2</sub> )
	Fluoroanilinium salts		
	2-fluoro-	1.4	1,2-C <sub>6</sub> H <sub>4</sub> F (NH <sub>3</sub> <sup>+</sup> )
	3-fluoro-	0.2	1,3-C <sub>6</sub> H <sub>4</sub> F (NH <sub>3</sub> <sup>+</sup> )
	4-fluoro-	0	1,4-C <sub>6</sub> H <sub>4</sub> F (NH <sub>3</sub> <sup>+</sup> )

## **$^{19}\text{F}$ CHEMICAL SHIFT RANGES**

The following table lists the  $^{19}\text{F}$  chemical shift ranges (in ppm) relative to neat  $\text{CFCl}_3$ .<sup>1-4</sup>

### **REFERENCES**

1. Yoder, C.H. and Schaeffer, C.D., Jr., *Introduction to Multinuclear NMR: Theory and Application*, Benjamin/Cummings, Menlo Park, CA, 1987.
2. <http://nmrsgl.chem.indiana.edu/NMRguidemisc/19Fshifts.html>.
3. Dungan, C.H. and Van Wazer, I.R., *Compilation of Reported  $^{19}\text{F}$  Chemical Shifts 1951 to Mid 1967*, Wiley Interscience, New York, 1970.
4. Emsley, J.W., Phillips, L., and Wray, V., *Fluorine Coupling Constants*, Pergamon, New York, 1977.

**$^{19}\text{F}$  Chemical Shift Ranges**

<b>Compound Type</b>	<b>Chemical Shift Range (ppm) Relative to Neat <math>\text{CFCl}_3</math></b>
$\text{F}-\text{C}(=\text{O})$	-70 to -20
$-\text{CF}_3$	+40 to +80
$>\text{CF}_2$	+80 to +140
$-\text{O}-\text{CF}$	+140 to +250
$\text{Ar}-\text{F}$	+80 to +170
Ar = aromatic moiety	

## **$^{19}\text{F}$ CHEMICAL SHIFTS OF SOME FLUORINE-CONTAINING COMPOUNDS**

The following table lists the  $^{19}\text{F}$  chemical shifts of some fluorine-containing compounds relative to neat  $\text{CFCl}_3$ . All chemical shifts are those of neat samples, and the values pertain to the fluorine present in the molecule.<sup>1-3</sup>

### **REFERENCES**

1. <http://nmrsg1.chem.indiana.edu/NMRguidemisc/19Fshifts.html>, 2003.
2. Dungan, C.H. and Van Wazer, I.R., *Compilation of Reported  $^{19}\text{F}$  Chemical Shifts 1951 to Mid 1967*, Wiley Interscience, New York, 1970.
3. Emsley, J.W., Phillips, L., and Wray, V., *Fluorine Coupling Constants*, Pergamon, New York, 1977.

**<sup>19</sup>F Chemical Shifts of Some  
Fluorine-Containing Compounds**

Compound	Chemical Shift (ppm)
CFCl <sub>3</sub>	0.00
CF <sub>4</sub>	-62.3
CH <sub>3</sub> F	-271.9
CF <sub>3</sub> H	-78.6
CF <sub>3</sub> R	-60 to -70
CF <sub>2</sub> H <sub>2</sub>	-143.6
CH <sub>3</sub> CH <sub>2</sub> F	-231
FCH=CH <sub>2</sub>	-114
CF <sub>2</sub> =CH <sub>2</sub>	- 81.3
CF <sub>2</sub> =CF <sub>2</sub>	-135
CF <sub>3</sub> COOH	-78.5
CF <sub>3</sub> COOC <sub>6</sub> H <sub>5</sub>	-73.85
CF <sub>3</sub> COOCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	-75.02
CF <sub>3</sub> COOCH <sub>3</sub>	-74.21
CF <sub>3</sub> COOCH <sub>2</sub> CH <sub>3</sub>	-78.7
C <sub>6</sub> F <sub>6</sub>	-164.9
C <sub>6</sub> F <sub>5</sub> H	-113.5
<i>p</i> -C <sub>6</sub> H <sub>4</sub> F <sub>2</sub>	-106.0
C <sub>6</sub> H <sub>5</sub> -CH <sub>2</sub> F	-207
C <sub>6</sub> H <sub>5</sub> -CF <sub>3</sub>	-63.72
C <sub>4</sub> F <sub>8</sub>	-135.15
C <sub>5</sub> F <sub>10</sub>	-132.9
CHF <sub>2</sub> OR	-82
(CF <sub>3</sub> ) <sub>2</sub> CO	-84.6
F <sub>2</sub>	+422.92
CF <sub>3</sub> Cl	-28.6
ClF <sub>3</sub>	+116, -4
ClF <sub>5</sub>	+247, +412
CF <sub>2</sub> Cl <sub>2</sub>	-8
CFCl <sub>2</sub> -CFCl <sub>2</sub>	-67.8
CFBr <sub>3</sub>	+7.38
CF <sub>2</sub> Br <sub>2</sub>	+7
IF <sub>7</sub>	+170
AsF <sub>3</sub>	-40.6
AsF <sub>5</sub>	-66
BF <sub>3</sub>	-131.3
(CH <sub>3</sub> ) <sub>2</sub> O.BF <sub>3</sub>	-158.3
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O.BF <sub>3</sub>	-153
SF <sub>6</sub>	+57.42
SO <sub>2</sub> F	-78.5
SbF <sub>5</sub>	-108
SeF <sub>6</sub>	+55
SiF <sub>4</sub>	-163.3
TeF <sub>6</sub>	-57
SF <sub>6</sub>	-57
XeF <sub>2</sub>	+258
XeF <sub>4</sub>	+438
XeF <sub>6</sub>	+550
NF <sub>3</sub>	+147
POF <sub>3</sub>	-90.7
PF <sub>3</sub>	-67.5

## FLUORINE COUPLING CONSTANTS

The following table gives the most important fluorine coupling constants, namely,  $J_{\text{FN}}$ ,  $J_{\text{FCF}}$ , and  $J_{\text{CF}}$ , together with some typical examples.<sup>1-9</sup> The coupling constant values vary with the solvent used.<sup>3</sup> The book by Emsley et al.<sup>1</sup> gives a complete, detailed list of various compounds.

## REFERENCES

1. Emsley, J.W., Phillips, L., and Wray, V., *Fluorine Coupling Constants*, Pergamon Press, Oxford, 1977.
2. Lambert, J.R., Shurvell, H.F., Verbit, L., Cooks, R.G., and Stout, G.H., *Organic Structural Analysis*, Macmillan, New York, 1976.
3. Yoder, C.H. and Schaeffer, C.D., Jr., *Introduction to Multinuclear NMR: Theory and Application*, Benjamin/Cummings, Menlo Park, CA, 1987.
4. Schaeffer, T., Marat, K., Peeling, J., and Veregin, R.P., Signs and mechanisms of  $^{13}\text{C}$ ,  $^{19}\text{F}$  spin-spin coupling constants in benzotrifluoride and its derivatives, *Can. J. Chem.*, 61, 2779, 1983.
5. Adcock, W. and Kok, G.B., Polar substituent effects on  $^{19}\text{F}$  chemical shifts of aryl and vinyl fluorides: a fluorine-19 nuclear magnetic resonance study of some 1,1-difluoro-2-(4-substituted-bicyclo[2,2,2]oct-1-yl)ethenes, *J. Org. Chem.*, 50, 1079, 1985.
6. Newmark, R.A. and Hill, J.R., Carbon-13-fluorine-19 coupling constants in benzotrifluorides, *Org. Magn. Reson.*, 9, 589, 1977.
7. Adcock, W. and Abeywickrema, A.N., Concerning the origin of substituent-induced fluorine-19 chemical shifts in aliphatic fluorides: carbon-13 and fluorine-19 nuclear magnetic resonance study of 1-fluoro-4-phenylbicyclo[2,2,2]octanes substituted in the arene ring, *J. Org. Chem.*, 47, 2945, 1982.
8. Dungan, C.H. and Van Wazer, I.R., *Compilation of Reported  $^{19}\text{F}$  Chemical Shifts 1951 to Mid 1967*, Wiley Interscience, New York, 1970.
9. Emsley, J.W., Phillips, L., and Wray, V., *Fluorine Coupling Constants*, Pergamon Press, New York, 1977.

**<sup>19</sup>F–H Coupling Constants**

Fluorinated Family	J <sub>FH</sub>	Example
<b>Two Bond</b>		
Alkanes	45–80	CH <sub>3</sub> F (45); CH <sub>2</sub> F <sub>2</sub> (50); CHF <sub>3</sub> (79); C <sub>2</sub> H <sub>5</sub> F (47); CH <sub>3</sub> CHF <sub>2</sub> (57); CH <sub>2</sub> FCH <sub>2</sub> F (48); CH <sub>2</sub> FCHF <sub>2</sub> (54); CF <sub>3</sub> CH <sub>2</sub> F (45); CF <sub>2</sub> HCF <sub>2</sub> CF <sub>3</sub> (52)
Alkyl chlorides	49–65	FCI <sub>2</sub> CH (53); CF <sub>2</sub> HCl (63); FCHCl–CHCl <sub>2</sub> (49); FCH <sub>2</sub> –CH <sub>2</sub> Cl (46)
Alkyl bromides	45–50	FBrCHCH <sub>3</sub> (50.5); FH <sub>2</sub> C–CH <sub>2</sub> Br (46); FBrCH–CHFBr (49)
Alkenes	45–80	FHC=CHF ( <i>cis</i> , 71.7; <i>trans</i> , 75.1); CH <sub>2</sub> =CHF (85); CF <sub>2</sub> =CHF (70.5); FCH <sub>2</sub> CH=CH <sub>2</sub> (47.5)
Aromatics	45–75	Cl–C <sub>6</sub> H <sub>4</sub> –CH <sub>2</sub> F (m-47, p-48); FH <sub>2</sub> C–C <sub>6</sub> H <sub>4</sub> –NO <sub>2</sub> (m-47, p-48); FH <sub>2</sub> C–C <sub>6</sub> H <sub>4</sub> –F (m-48, p-48); p-Br–C <sub>6</sub> H <sub>4</sub> –OCF <sub>2</sub> H (73)
Ethers	40–75	FH <sub>2</sub> COCH <sub>3</sub> (74); CF <sub>2</sub> HCF <sub>2</sub> OCH <sub>3</sub> (46); F <sub>2</sub> HC–O–CH(CH <sub>3</sub> ) <sub>2</sub> (75)
Ketones	45–50	FCH <sub>2</sub> COCH <sub>3</sub> (47); F <sub>2</sub> HC–COCH <sub>3</sub> (54); CH <sub>3</sub> CH <sub>2</sub> CHFCOCH <sub>3</sub> (50); F <sub>2</sub> HC–COCH(CF <sub>3</sub> ) <sub>2</sub> (54)
Aldehydes	~50	CH <sub>3</sub> CH <sub>2</sub> CHFCHO (51)
Esters	45–70	CFH <sub>2</sub> CO <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> (47); CH <sub>3</sub> CHFCO <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> (48)
<b>Three Bond</b>		
Alkanes	2–25	CF <sub>2</sub> HCH <sub>3</sub> (21); (CH <sub>3</sub> ) <sub>3</sub> CF (20.4); CH <sub>3</sub> CHFCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> (23); CF <sub>3</sub> CH <sub>3</sub> (13)
Alkyl chlorides	8–20	CF <sub>2</sub> HCHCl <sub>2</sub> (8); CF <sub>2</sub> ClCH <sub>3</sub> (15)
Alkyl bromides	15–25	CF <sub>2</sub> BrCH <sub>2</sub> Br (22); CF <sub>2</sub> BrCH <sub>3</sub> (16); FC(CH <sub>3</sub> ) <sub>2</sub> CHBrCH <sub>3</sub> (21)
Alkenes	–5 to 60 J <sub>HCF</sub> ( <i>cisoid</i> ), <20 J <sub>HCF</sub> ( <i>transoid</i> ), >20	CHF=CHF ( <i>cis</i> , 19.6; <i>trans</i> , 2.8); CH <sub>2</sub> =CHF ( <i>cis</i> , 19.6; <i>trans</i> , 51.8); CHF=CF <sub>2</sub> ( <i>cis</i> , –4.2; <i>trans</i> , 12.5); CH <sub>2</sub> =CF <sub>2</sub> ( <i>cis</i> , 0.6; <i>trans</i> , 33.8)
Alcohols	5–30	CF <sub>3</sub> CH <sub>2</sub> OH (8); FCH <sub>2</sub> CH <sub>2</sub> OH (29); CH <sub>3</sub> CHFCH <sub>2</sub> OH (23.6, 23.6); CF <sub>3</sub> CH(OH)CH <sub>3</sub> (7.5); CF <sub>3</sub> CH(OH)CF <sub>3</sub> (6); FC(CH <sub>3</sub> ) <sub>2</sub> C(OH)(CH <sub>3</sub> ) <sub>2</sub> (23)
Ketones	5–25	CH <sub>3</sub> CH <sub>2</sub> CHFCOCH <sub>3</sub> (24); FC(CH <sub>3</sub> ) <sub>2</sub> COCH <sub>3</sub> (21); (CF <sub>3</sub> ) <sub>2</sub> CHCOCH <sub>3</sub> (8); CF <sub>2</sub> HCOCH(CF <sub>3</sub> ) <sub>2</sub> (7)
Aldehydes	10–25	(CH <sub>3</sub> ) <sub>2</sub> CFCHO (22)
Esters	10–25	CH <sub>3</sub> CHFCO <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> (23); (CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> CFCO <sub>2</sub> CH <sub>3</sub> (16.5)



<sup>19</sup> F– <sup>19</sup> F Coupling		
Carbon	J <sub>FCF</sub>	Examples
<b>Two Bond</b>		
Saturated (sp <sup>3</sup> )	140–250	CF <sub>3</sub> CF <sub>2</sub> <sup>a,b</sup> CFHCH <sub>3</sub> (J <sub>ab</sub> = 270); CF <sub>2</sub> <sup>a,b</sup> BrCHF <sub>2</sub> SO <sub>2</sub> F (J <sub>ab</sub> = 188); CH <sub>3</sub> O–CF <sub>2</sub> <sup>a,b</sup> CFH <sub>2</sub> SO <sub>2</sub> F (J <sub>ab</sub> = 147); CH <sub>3</sub> O–CF <sub>2</sub> <sup>a,b</sup> CFHCl (J <sub>ab</sub> = 142); CH <sub>3</sub> S–CF <sub>2</sub> <sup>a,b</sup> CFHCl (J <sub>ab</sub> = 222)
Cycloalkanes	150–240	F <sub>2</sub> C(CH <sub>2</sub> ) <sub>2</sub> (150) (three-membered) F <sub>2</sub> C(CH <sub>2</sub> ) <sub>3</sub> (200) (four-membered) F <sub>2</sub> C(CH <sub>2</sub> ) <sub>4</sub> (240) (five-membered) F <sub>2</sub> C(CH <sub>2</sub> ) <sub>5</sub> (228) (six-membered)
Unsaturated (sp <sup>2</sup> )	≤100	CF <sub>2</sub> =CH <sub>2</sub> (31, 36); CF <sub>2</sub> =CHF (87); CF <sub>2</sub> =CBrCl (30); CF <sub>2</sub> =CHCl (41); CF <sub>2</sub> =CFBr (75); CF <sub>2</sub> =NCF <sub>3</sub> (82); CF <sub>2</sub> =CFCN (27); CF <sub>2</sub> =CFCOF (7); CF <sub>2</sub> =CFOCH <sub>2</sub> CF <sub>3</sub> (102); CF <sub>2</sub> =CBrCH <sub>2</sub> N(CF <sub>3</sub> ) <sub>2</sub> (30); CF <sub>2</sub> =CFCOCF <sub>2</sub> CF <sub>3</sub> (12); CF <sub>2</sub> =CHC <sub>6</sub> H <sub>5</sub> (33); CF <sub>2</sub> =CH(CH <sub>2</sub> ) <sub>5</sub> CH <sub>3</sub> (50); CF <sub>2</sub> =CH–Ar[Ar=aryl] (50)
<b>Three Bond</b>		
Saturated (sp <sup>3</sup> )	0–16	CF <sub>3</sub> CH <sub>2</sub> F (16); CF <sub>3</sub> CF <sub>3</sub> (3.5); CF <sub>3</sub> CHF <sub>2</sub> (3); CH <sub>2</sub> FCH <sub>2</sub> F (10–12); CF <sub>2</sub> <sup>a</sup> HCF <sup>b</sup> HCF <sub>2</sub> H (J <sub>ab</sub> = 13); CF <sub>2</sub> HCF <sub>2</sub> <sup>a</sup> CH <sub>2</sub> F (J <sub>ab</sub> = 14); CF <sub>3</sub> <sup>a</sup> CF <sub>2</sub> <sup>b</sup> CF <sup>c</sup> HCH <sub>3</sub> (J <sub>ab</sub> < 1; J <sub>bc</sub> = 15); CF <sub>3</sub> <sup>a</sup> CF <sup>b</sup> HCF <sub>2</sub> <sup>c</sup> H (J <sub>ab</sub> = 12; J <sub>bc</sub> = 12); CF <sub>3</sub> <sup>a</sup> CF <sub>2</sub> <sup>b</sup> C≡CF <sub>3</sub> (J <sub>ab</sub> = 3.3); CF <sub>3</sub> <sup>a</sup> CF <sub>2</sub> <sup>b</sup> C≡CCF <sub>3</sub> (J <sub>ab</sub> = 3.3); (CF <sub>3</sub> <sup>a</sup> ) <sub>2</sub> CF <sup>b</sup> C≡CCl (J <sub>ab</sub> = 10); CF <sub>3</sub> CF <sub>2</sub> COCH <sub>2</sub> CH <sub>3</sub> (1); FCH <sub>2</sub> CFHCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> (–11.6); CF <sub>3</sub> <sup>a</sup> CF <sub>2</sub> <sup>b</sup> CF <sub>2</sub> <sup>c</sup> COOH (J <sub>ab</sub> < 1; J <sub>bc</sub> < 1); (CF <sub>3</sub> <sup>a</sup> ) <sub>2</sub> CF <sup>b</sup> SO(OC <sub>2</sub> H <sub>5</sub> ) (J <sub>ab</sub> = 8)
Unsaturated (sp <sup>2</sup> )	>30	FCH=CHF ( <i>cis</i> , –18.7; <i>trans</i> , –133.5); CF <sub>2</sub> =CHBr (34.5); CF <sub>2</sub> =CHCl (41); CF <sub>2</sub> =CH <sub>2</sub> (37)

<b>C–<sup>19</sup>F Coupling</b>		
Fluorinated Family	J <sub>CF</sub> , H <sub>2</sub>	Examples
<b>One Bond</b>		
Alkanes	150–290	CH <sub>3</sub> F (158); CH <sub>2</sub> F <sub>2</sub> (237); CHF <sub>3</sub> (274); CF <sub>4</sub> (257); CF <sub>3</sub> CF <sub>3</sub> (281); CF <sub>3</sub> CH <sub>3</sub> (271); (CH <sub>3</sub> ) <sub>3</sub> CF (167); (C <sup>a</sup> F <sub>3</sub> <sup>b</sup> ) <sub>2</sub> C <sup>c</sup> F <sub>2</sub> <sup>d</sup> (J <sub>ab</sub> = 285; J <sub>cd</sub> = 265)
Alkenes	250–300	CF <sub>2</sub> =CD <sub>2</sub> (287); CF <sub>2</sub> =CCl <sub>2</sub> (–289); CF <sub>2</sub> =CBr <sub>2</sub> (290); ClFC=CHCl ( <i>cis</i> , –300; <i>trans</i> , –307); ClFC=CClF ( <i>cis</i> , 290; <i>trans</i> , 290)
Alkynes	250–260	C <sup>a</sup> F <sub>3</sub> <sup>b</sup> C≡CF (J <sub>ab</sub> = 259); CF <sub>3</sub> C≡CCF <sub>3</sub> (256)
Alkyl chlorides	275–350	CFCl <sub>3</sub> (337); CF <sub>2</sub> Cl <sub>2</sub> (325); CF <sub>3</sub> Cl (299); CF <sub>3</sub> (CCl <sub>2</sub> ) <sub>2</sub> CF <sub>3</sub> (286); CF <sub>3</sub> CH <sub>2</sub> Cl (274); CF <sub>3</sub> CCl=CCl <sub>2</sub> (274); CF <sub>2</sub> =CCl <sub>2</sub> (–289); CF <sub>3</sub> CCl <sub>3</sub> (283)
Alkyl bromides	290–375	CFBr <sub>3</sub> (372); CF <sub>2</sub> Br <sub>2</sub> (358); CF <sub>3</sub> Br (324); CF <sub>3</sub> CH <sub>2</sub> Br (272); CF <sub>2</sub> =CBr <sub>2</sub> (290)
Acyl fluorides	350–370	HCOF (369); CH <sub>3</sub> COF (353)
Carboxylic acids	245–290	CF <sub>3</sub> COOH (283); CF <sub>2</sub> HCO <sub>2</sub> H (247)
Alcohols	~275	CF <sub>3</sub> CH <sub>2</sub> OH (278)
Nitriles	~250	CF <sub>2</sub> HCN (244)
Esters	~285	CF <sub>3</sub> CO <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> (284)
Ketones	~290	CF <sub>3</sub> COCH <sub>3</sub> (289)
Ethers	~265	(CF <sub>3</sub> ) <sub>2</sub> O (265)

## RESIDUAL PEAKS OBSERVED IN THE $^1\text{H}$ NMR SPECTRA OF COMMON DEUTERATED ORGANIC SOLVENTS

The following table lists the residual peaks that are observed in the  $^1\text{H}$  NMR spectra of common deuterated organic solvents. These peaks are generally attributed to the nondeuterated parent compound that serves as an impurity and are marked with an asterisk. In addition, other less significant peaks often arise due to other impurities.

Together with the formula and molecular weight, the table lists the expected chemical shifts,  $\delta$ ; multiplicities; and, when possible, the coupling constant,  $J_{\text{HD}}$ , for every solvent. All spectra are at least 99.5% deuterium pure.<sup>1-5</sup>

### REFERENCES

1. Yoder, C.H. and Schaeffer, C.D., Jr., *Introduction to Multinuclear NMR*, Benjamin Cummings, Menlo Park, CA, 1987.
2. Silverstein, R.M. and Webster, F.X., *Spectrometric Identification of Organic Compounds*, 6th ed., John Wiley & Sons, New York, 1998.
3. Gunther, H., *NMR Spectroscopy: Basic Principles, Concepts and Applications in Chemistry*, John Wiley & Sons, New York, 2003.
4. Lambert, J.B., Holland, L.N., and Mazzola, E.P., *Nuclear Magnetic Resonance Spectroscopy: Introduction to Principles, Applications and Experimental Methods*, Prentice Hall, Englewood Cliffs, NJ, 2003.
5. Nelson, J.H., *Nuclear Magnetic Resonance Spectroscopy*, 2nd ed., John Wiley & Sons, New York, 2003.

**Residual Peaks Observed in the <sup>1</sup>H NMR Spectra of Common  
Deuterated Organic Solvents**

Solvent	Formula	Molecular Weight	δ (mult) <sup>a</sup>	J <sub>HD</sub>
Acetic acid-d <sub>4</sub>	CD <sub>3</sub> COOD	64.078	*11.53 (1) *2.03 (5)	2
Acetone-d <sub>6</sub>	(CD <sub>3</sub> ) <sub>2</sub> C=O	64.117	*2.04 (5) 2.78 (1) 2.82 (1)	2.2
Acetonitrile-d <sub>3</sub>	CD <sub>3</sub> CN	44.017	*1.93 (5) 2.1–2.15 2.2–2.4	2.5
Benzene-d <sub>6</sub>	C <sub>6</sub> D <sub>6</sub>	84.153	*7.12 (b)	
Chloroform-d <sub>3</sub>	CDCl <sub>3</sub>	120.384	1.55 <sup>b</sup> 1.60 <sup>b</sup> 7.2 *7.24 (1)	
Cyclohexane-d <sub>12</sub>	(CD <sub>2</sub> ) <sub>6</sub>	96.236	*1.38 (b)	
Deuterium oxide	D <sub>2</sub> O	20.028	*4.63 (b) <sup>c</sup> *4.67 (b) <sup>d</sup>	
1,2-Dichloroethane-d <sub>4</sub>	CD <sub>2</sub> ClCD <sub>2</sub> Cl	102.985	*3.72 (b)	
Dichloromethane-d <sub>2</sub>	See Methylene chloride-d <sub>2</sub>			
Diethylene glycol dimethylether-d <sub>14</sub>	See Diglyme-d <sub>14</sub>			
Diethylether-d <sub>10</sub>	(CD <sub>3</sub> CD <sub>2</sub> ) <sub>2</sub> O	84.185	*3.34 (m) *1.07 (m)	
Diglyme-d <sub>14</sub>	CD <sub>3</sub> O(CD <sub>2</sub> ) <sub>2</sub> O(CD <sub>2</sub> ) <sub>2</sub> OCD <sub>3</sub>	148.263	*3.49 (b) *3.40 (b) *3.22 (5)	1.5
<i>N,N</i> -Dimethylformamide-d <sub>7</sub>	DCON(CD <sub>3</sub> ) <sub>2</sub>	80.138	*8.01 (b) *2.91 (5) *2.74 (5)	2 2
Dimethylsulfoxide-d <sub>6</sub>	(CD <sub>3</sub> ) <sub>2</sub> SO		3.3–3.4 *2.49 (5)	1.7
1,2-Diethoxyethane-d <sub>10</sub>	See Glyme-d <sub>10</sub>			
<i>p</i> -Dioxane-d <sub>8</sub>	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	96.156	*3.53 (m)	
Ethanol-d <sub>6</sub> (anhydrous)	CD <sub>3</sub> CD <sub>2</sub> OD	52.106	*5.19 (1) *3.55 (b) *1.11 (m)	
Glyme-d <sub>10</sub>	CD <sub>2</sub> OCD <sub>2</sub> CD <sub>2</sub> OCD <sub>3</sub>	100.184	*3.40 (m) *3.22 (5)	1.6
Hexamethylphosphoric triamide-d <sub>18</sub> (HMPT-d <sub>18</sub> )	[(CD <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> P=O	197.314	*2.53 (m)	
Methanol-d <sub>4</sub>	CD <sub>3</sub> OH	36.067	*4.78 (1) *3.30 (5)	1.7
Methylene chloride-d <sub>2</sub>	CD <sub>2</sub> Cl <sub>2</sub>	86.945	*5.32 (3) 1.4–1.5 (b)	1
Nitrobenzene-d <sub>5</sub>	C <sub>6</sub> D <sub>5</sub> NO <sub>2</sub>	128.143	*8.11 (b) *7.67 (b) *7.50 (b)	
Nitromethane-d <sub>3</sub>	CD <sub>3</sub> NO <sub>2</sub>	64.059	*4.33 (5)	2
2-Propanol-d <sub>8</sub>	(CD <sub>3</sub> ) <sub>2</sub> CDOD	68.146	*5.12 (1) *3.89 (b) *1.10 (b)	
Pyridine-d <sub>5</sub>	C <sub>6</sub> D <sub>5</sub> N	84.133	*8.71 (b) *7.55 (b) *7.19 (b) 4.8 <sup>b</sup> 4.9 <sup>b</sup>	

**Residual Peaks Observed in the  $^1\text{H}$  NMR Spectra of Common  
Deuterated Organic Solvents (continued)**

<b>Solvent</b>	<b>Formula</b>	<b>Molecular Weight</b>	<b><math>\delta</math> (mult)<sup>a</sup></b>	<b><math>J_{\text{HD}}</math></b>
Tetrahydrofuran- $\text{d}_8$	$\text{C}_4\text{D}_8\text{O}$	80.157	*3.58 (b) 2.4 <sup>b</sup> 2.3 <sup>b</sup> *1.73 (b)	
Toluene- $\text{d}_8$	$\text{C}_6\text{D}_5\text{CD}_3$	100.191	*7.09 (m) *7.00 (b) *6.98 (m) *2.09 (5)	2.3
Trifluoroacetic acid- $\text{d}$	$\text{CF}_3\text{COOD}$	115.030	*11.50 (1)	

<sup>a</sup> Chemical shift,  $\delta$ , in ppm; mult = multiplicity (indicated by a number); b = broad, m = multiplet.

<sup>b</sup> Two peaks that may often appear as one broad peak.

<sup>c</sup> When DSS, 3-(trimethylsilyl)-1-propane sulfonic acid, sodium salt, is used as a reference standard.

<sup>d</sup> When TSP, sodium-3-trimethylpropionate, is used as a reference standard.

## CHAPTER 10

# Mass Spectrometry

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## NATURAL ABUNDANCE OF IMPORTANT ISOTOPES

The following table lists the atomic masses and relative percent concentrations of naturally occurring isotopes of importance in mass spectrometry.<sup>1-5</sup>

### REFERENCES

1. deHoffmann, E. and Stroobant, V., *Mass Spectrometry: Principles and Applications*, 2nd ed., John Wiley & Sons, Chichester, U.K., 2001.
2. Johnstone, R.A.W. and Rose, M.E., *Mass Spectrometry for Chemists and Biochemists*, Cambridge University Press, Cambridge, U.K., 1996.
3. Lide, D.R., Ed., *CRC Handbook of Chemistry and Physics*, 83rd ed., CRC Press, Boca Raton, FL, 2002.
4. McLafferty, F.W. and Turecek, F., *Interpretation of Mass Spectra*, 4th ed., University Science Books, Mill Valley, CA, 1993.
5. Watson, J.T., *Introduction to Mass Spectrometry*, 3rd ed., Lippincott-Raven, Philadelphia, 1997.

**Natural Abundance of Important Isotopes**

Element	Total No. of Isotopes	More Prominent Isotopes (Mass, Percent Abundance)		
Hydrogen	3	<sup>1</sup> H (1.00783, 99.985)	<sup>2</sup> H (2.01410, 0.015)	
Boron	6	<sup>10</sup> B (10.01294, 19.8)	<sup>11</sup> B (11.00931, 80.2)	
Carbon	7	<sup>12</sup> C (12.00000, 98.9)	<sup>13</sup> C (13.00335, 1.1)	
Nitrogen	7	<sup>14</sup> N (14.00307, 99.6)	<sup>15</sup> N (15.00011, 0.4)	
Oxygen	8	<sup>16</sup> O (15.99491, 99.8)		<sup>18</sup> O (17.9992, 0.2)
Fluorine	6	<sup>19</sup> F (18.99840, ≈100.0)		
Silicon	8	<sup>28</sup> Si (27.97693, 92.2)	<sup>29</sup> Si (28.97649, 4.7)	<sup>30</sup> Si (29.97376, 3.1)
Phosphorus	7	<sup>31</sup> P (30.97376, ≈100.0)		
Sulfur	10	<sup>32</sup> S (31.972017, 95.0)	<sup>33</sup> S (32.97146, 0.7)	<sup>34</sup> S (33.96786, 4.2)
Chlorine	11	<sup>35</sup> Cl (34.96885, 75.5)		<sup>37</sup> Cl (36.96590, 24.5)
Bromine	17	<sup>79</sup> Br (78.9183, 50.5)		<sup>81</sup> Br (80.91642, 49.5)
Iodine	23	<sup>127</sup> I (126.90466, ≈100.0)		

## RULES FOR DETERMINATION OF MOLECULAR FORMULA

The following rules are used in the mass spectrometric determination of the molecular formula of an organic compound.<sup>1-5</sup> These rules should be applied to the molecular ion peak and its isotopic cluster. The molecular ion, in turn, is usually the highest mass in the spectrum. It must be an odd-electron ion and must be capable of yielding all other important ions of the spectrum via a logical neutral species loss. The elements that are assumed to possibly be present on the original molecule are carbon, hydrogen, nitrogen, the halogens, sulfur, and oxygen. The molecular formula that can be derived is not the only possible one, and consequently, information from nuclear magnetic resonance spectrometry and infrared spectrophotometry is necessary for the final molecular formula determination.

Modern mass spectral databases allow the automated searching of very extensive mass spectral libraries.<sup>6</sup> This has made the identification of compounds by mass spectrometry a far more straightforward task. One must understand, however, that such databases are no substitute for the careful analysis of each mass spectrum and that the results of database matchup are merely suggestions.

## REFERENCES

1. Lee, T.A., *A Beginner's Guide to Mass Spectral Interpretation*, Wiley, New York, 1998.
2. McLafferty, F.W., *Interpretation of Mass Spectra*, University Science Books, Mill Valley, CA, 1993.
3. Shrader, S.R., *Introductory Mass Spectrometry*, Allyn and Bacon, Boston, 1971.
4. Smith, R.M., *Understanding Mass Spectra: A Basic Approach*, Wiley, New York, 1999.
5. Watson, J.T. and Watson, T.J., *Introduction to Mass Spectrometry*, Lippincott, Williams & Wilkins, Philadelphia, 1998.
6. NIST Standard Reference Database 1A, NIST/EPA/NIH Mass Spectral Library with Search Program (Data Version: NIST '02, Software Version 2.0).

**Rule 1:** An odd molecular ion value suggests the presence of an odd number of nitrogen atoms; an even molecular ion value is due to the presence of zero, or an even number of nitrogen atoms. Thus,  $m/e = 141$  suggests 1, 3, 5, 7, etc., nitrogen atoms, while  $m/e = 142$  suggests 0, 2, 4, 6, etc., nitrogen atoms.

**Rule 2:** The maximum number of carbons ( $N_C^{\max}$ ) can be calculated from the formula

$$(N_C^{\max}) = \frac{\text{Relative intensity of } M+1 \text{ peak}}{\text{Relative intensity of } M^+ \text{ peak}} \times \frac{100}{1.1}$$

where  $M+1$  is the peak one unit above the value of the molecular ion ( $M^+$ ). This rule gives the *maximum* number of carbons, but not necessarily the *actual* number. If, for example, the relative intensities of  $M^+$  and  $M+1$  are 100 and 9% respectively, then the maximum number of carbons is

$$(N_C^{\max}) = (9/100) \times (100 / 1.1) = 8$$

In this case there is a possibility for seven, six, etc., carbons, but not for nine or more.

**Rule 3:** The maximum numbers of sulfur atoms ( $N_s^{\max}$ ) can be calculated from the formula

$$(N_s^{\max}) = \frac{\text{Relative intensity of } M+2 \text{ peak}}{\text{Relative intensity of } M^+ \text{ peak}} \times \frac{100}{4.4}$$

where  $M + 2$  is the peak two units above that of the molecular ion  $M^+$ .

**Rule 4:** The actual number of chlorine and bromine atoms can be derived from the table that follows later in this chapter.

**Rule 5:** The difference should be only oxygen and hydrogen atoms. These rules assume the absence of phosphorus, silicon, or any other elements.



## NEUTRAL MOIETIES EJECTED FROM SUBSTITUTED BENZENE RING COMPOUNDS

The following table lists the most common substituents encountered in benzene rings and the neutral particles lost and observed on the mass spectrum.<sup>1</sup> Complex rearrangements are often encountered and enhanced by the presence of one or more heteroatomic substituent(s) in the aromatic compound. All neutral particles that are not the product of rearrangement appear in parentheses and are produced alongside the species that are formed via rearrangement. Prediction of the more abundant moiety is not easy, as it is seriously affected by factors that dictate the nature of the compound. These include the nature and the position of any other substituents, as well as the stability of any intermediate(s) formed. Correlations of the data with the corresponding Hammett  $\sigma$  constants have been neither consistent nor conclusive.

### REFERENCES

1. Rose, M.E. and Johnstone, R.A.W., *Mass Spectroscopy for Chemists and Biochemists*, Cambridge University Press, Cambridge, U.K., 1982.

Neutral Moieties Ejected from Substituted Benzene Ring Compounds	
Substituent	Neutral Moieties Ejected after Rearrangement
NO <sub>2</sub>	NO, CO, (NO <sub>2</sub> )
NH <sub>2</sub>	HCN
NHCOCH <sub>3</sub>	C <sub>2</sub> H <sub>2</sub> O, HCN
CN	HCN
F	C <sub>2</sub> H <sub>2</sub>
OCH <sub>3</sub>	CH <sub>2</sub> O, CHO, CH <sub>3</sub>
OH	CO, CHO
SO <sub>2</sub> NH <sub>2</sub>	SO <sub>2</sub> , HCN
SH	CS, CHS (SH)
SCH <sub>3</sub>	CS, CH <sub>2</sub> S, SH, (CH <sub>3</sub> )

## ORDER OF FRAGMENTATION INITIATED BY THE PRESENCE OF A SUBSTITUENT ON A BENZENE RING

The following table lists the relative order of ease of fragmentation that is initiated by the presence of a substituent in the benzene ring in mass spectrometry.<sup>1</sup> The ease of fragmentation decreases from top to bottom. The substituents marked with an asterisk are very similar in their ease of fragmentation. Particularly in the case of disubstituted benzene rings, the order of fragmentation at the substituent linkage may be easily predicted using this table. As a rule of thumb, the more complex the size of the substituent, the easier is its decomposition. For instance, in all chloroacetophenone isomers (1,2-, 1,3-, or 1,4-), the elimination of the methyl radical occurs before the loss of chlorine. On the other hand, under normal mass conditions, all bromofluorobenzenes (1,2-, 1,3-, and 1,4-) easily lose the bromine but not the fluorine. Deuterium labeling studies have indicated that any rearrangement of the benzene compounds occurs in the molecular ion and before fragmentation.

### REFERENCES

1. Rose, M.E. and Johnstone, R.A.W., *Mass Spectroscopy for Chemists and Biochemists*, Cambridge University Press, Cambridge, U.K., 1982.

**Order of Fragmentation Initiated by the Presence  
of a Substituent on a Benzene Ring**

Substituent	Neutral Moiety Eliminated
COCH <sub>3</sub>	CH <sub>3</sub>
CO <sub>2</sub> CH <sub>3</sub>	OCH <sub>3</sub>
NO <sub>2</sub>	NO <sub>2</sub>
*I	I
*OCH <sub>3</sub>	CH <sub>2</sub> O, CHO
*Br	Br
OH	CO, CHO
CH <sub>3</sub>	H
Cl	Cl
NH <sub>2</sub>	HCN
CN	HCN
F	C <sub>2</sub> H <sub>2</sub>

## CHLORINE–BROMINE COMBINATION ISOTOPE INTENSITIES

Due to the distinctive mass spectral patterns caused by the presence of chlorine and bromine in a molecule, interpretation of a mass spectrum can be much easier if the results of the relative isotopic concentrations are known. The following table provides peak intensities (relative to the molecular ion ( $M^+$ ) at an intensity normalized to 100%) for various combinations of chlorine and bromine atoms, assuming the absence of all other elements except carbon and hydrogen.<sup>1–4</sup> The mass abundance calculations were based on the most recent atomic mass data.<sup>1</sup>

### REFERENCES

1. Lide, D.R., *CRC Handbook of Chemistry and Physics*, 83rd ed., CRC Press, Boca Raton, FL, 2002.
2. McLafferty, F.W., *Interpretation of Mass Spectra*, 4th ed., University Science Books, Mill Valley, CA, 1993.
3. Silverstein, R.H., Bassler, G.C., and Morrill, T.C., *Spectroscopic Identification of Organic Compounds*, 6th ed., John Wiley & Sons, New York, 1998.
4. Williams, D.H. and Fleming, I., *Spectroscopic Methods in Organic Chemistry*, 4th ed., McGraw-Hill, London, 1989.

**Relative Intensities of Isotope Peaks for Combinations of Bromine and Chlorine ( $M^+ = 100\%$ )**

		<b>Br<sub>0</sub></b>	<b>Br<sub>1</sub></b>	<b>Br<sub>2</sub></b>	<b>Br<sub>3</sub></b>	<b>Br<sub>4</sub></b>
Cl <sub>0</sub>	P + 2		98.0	196.0	294.0	390.8
	P + 4			96.1	288.2	574.7
	P + 6				94.1	375.3
	P + 8					92.0
Cl <sub>1</sub>	P + 2	32.5	130.6	228.0	326.1	424.6
	P + 4		31.9	159.0	383.1	704.2
	P + 6			31.2	187.4	564.1
	P + 8				30.7	214.8
	P + 10					30.3
Cl <sub>2</sub>	P + 2	65.0	163.0	261.1	359.3	456.3
	P + 4	10.6	74.4	234.2	490.2	840.3
	P + 6		10.4	83.3	312.8	791.6
	P + 8			10.2	91.7	397.5
	P + 10				9.8	99.2
	P + 12					10.1
Cl <sub>3</sub>	P + 2	97.5	195.3	294.0	393.3	489
	P + 4	31.7	127.0	99.7	609.8	989
	P + 6	3.4	34.4	159.4	473.8	1064
	P + 8		3.3	37.1	193.9	654
	P + 10			3.2	39.6	229
	P + 12				3.0	42
	P + 14					3.2
Cl <sub>4</sub>	P + 2	130.0	228.3	326.6	4.2	522
	P + 4	63.3	190.9	414.9	735.3	1149
	P + 6	13.7	75.8	263.1	670.0	1388
	P + 8	1.2	14.4	88.8	347.1	1002
	P + 10		1.1	15.4	102.2	443
	P + 12			1.3	16.2	117
	P + 14				0.7	17
Cl <sub>5</sub>	P + 2	162.6	260.7	358.9		
	P + 4	105.7	265.3	520.8		
	P + 6	34.3	137.9	397.9		
	P + 8	5.5	39.3	174.5		
	P + 10	0.3	5.8	44.3		
	P + 12		0.3	5.7		
Cl <sub>6</sub>	P + 2	195.3				
	P + 4	158.6				
	P + 6	68.8				
	P + 8	16.6				
	P + 10	2.1				
	P + 12	0.1				
Cl <sub>7</sub>	P + 2	227.8				
	P + 4	222.1				
	P + 6	120.3				
	P + 8	39.0				
	P + 10	7.5				
	P + 12	0.8				
Cl <sub>7</sub>	P + 14	0.05				

## REFERENCE COMPOUNDS UNDER ELECTRON IMPACT CONDITIONS IN MASS SPECTROMETRY

The following table lists the most popular reference compounds for use under electron impact conditions in mass spectrometry. For accurate mass measurements, the reference compound is introduced and ionized concurrently with the sample and the reference peaks are resolved from sample peaks. Reference compounds should contain as few heteroatoms and isotopes as possible. This is to facilitate the assignment of reference masses and minimize the occurrence of unresolved multiplets within the reference spectrum.<sup>1</sup> An approximate upper mass limit should assist in the selection of the appropriate reference.<sup>1,2</sup>

### REFERENCES

1. Chapman, J.R., *Computers in Mass Spectrometry*, Academic Press, London, 1978.
2. Chapman, J.R., *Practical Organic Mass Spectrometry*, 2nd ed., John Wiley & Sons, Chichester, U.K., 1995.

**Reference Compounds under Electron Impact Conditions in Mass Spectrometry**

Reference Compound	Formula	Upper Mass Limit
Perfluoro-2-butyltetrahydrofuran	$C_8F_{16}O$	416
Decafluorotriphenyl phosphine (ultramark 443; DFTPP)	$(C_6F_5)_3P$	443
Heptacosafuorotributylamine (perfluoro tributylamine; heptacosa; PFTBA)	$(C_4F_9)_3N$	671
Perfluoro kerosene, low-boiling (perfluoro kerosene-L)	$CF_3(CF_2)_nCF_3$	600
Perfluoro kerosene, high-boiling (perfluoro kerosene-H)	$CF_3(CF_2)_nCF_3$	800–900
Tris (trifluoromethyl)-s-triazine	$C_3N_3(CF_3)_3$	285
Tris (pentafluoroethyl)-s-triazine	$C_3N_3(CF_2CF_3)_3$	435
Tris (heptafluoropropyl)-s-triazine	$C_3N_3(CF_2CF_2CF_3)_3$	585
Tris (perfluoroheptyl)-s-triazine	$C_3N_3[(CF_2)_6CF_3]_3$	1185
Tris (perfluorononyl)-s-triazine	$C_3N_3[(CF_2)_8CF_3]_3$	1485
Ultramark 1621 (fluoroalkoxy cyclotriphosphazine mixture)	$P_3N_3[OCH_2(CF_2)_nH]_6$	~2000
Fomblin diffusion pump fluid (ultramark F-series; perfluoropolyether)	$CF_3O[CF(CF_3)CF_2O]_m(CF_2O)_nCF_3$	≥3000

## MAJOR REFERENCE MASSES IN THE SPECTRUM OF HEPTACOSAFLUOROTRIBUTYLAMINE (PERFLUOROTRIBUTYLAMINE)

The following list tabulates the major reference masses (with their relative intensities and formulas) of the mass spectrum of heptacosafuorotributylamine.<sup>1</sup> This is one of the most widely used reference compounds in mass spectrometry.

### REFERENCES

1. Chapman, J.R., *Practical Organic Mass Spectrometry*, 2nd ed., John Wiley & Sons, Chichester, U.K., 1995.

**Major Reference Masses in the Spectrum of  
Heptacosafuorotributylamine (Perfluorotributylamine)**

Mass	Relative Intensity	Formula	Mass	Relative Intensity	Formula
613.9647	2.6	C <sub>12</sub> F <sub>24</sub> N	180.9888	1.9	C <sub>4</sub> F <sub>7</sub>
575.9679	1.7	C <sub>12</sub> F <sub>22</sub> N	175.9935	1.0	C <sub>4</sub> F <sub>6</sub> N
537.9711	0.4	C <sub>12</sub> F <sub>20</sub> N	168.9888	3.6	C <sub>3</sub> F <sub>7</sub>
501.9711	8.6	C <sub>9</sub> F <sub>20</sub> N	163.9935	0.7	C <sub>3</sub> F <sub>6</sub> N
463.9743	3.8	C <sub>9</sub> F <sub>18</sub> N	161.9904	0.3	C <sub>4</sub> F <sub>6</sub>
425.9775	2.5	C <sub>9</sub> F <sub>16</sub> N	149.9904	2.1	C <sub>3</sub> F <sub>6</sub>
413.9775	5.1	C <sub>8</sub> F <sub>16</sub> N	130.9920	31	C <sub>3</sub> F <sub>5</sub>
375.9807	0.9	C <sub>8</sub> F <sub>14</sub> N	118.9920	8.3	C <sub>2</sub> F <sub>5</sub>
325.9839	0.4	C <sub>7</sub> F <sub>12</sub> N	113.9967	3.7	C <sub>2</sub> F <sub>4</sub> N
313.9839	0.4	C <sub>6</sub> F <sub>12</sub> N	111.9936	0.7	C <sub>3</sub> F <sub>4</sub>
263.9871	10	C <sub>5</sub> F <sub>10</sub> N	99.9936	12	C <sub>2</sub> F <sub>4</sub>
230.9856	0.9	C <sub>5</sub> F <sub>9</sub>	92.9952	1.1	C <sub>3</sub> F <sub>3</sub>
225.9903	0.6	C <sub>5</sub> F <sub>8</sub> N	68.9952	100	CF <sub>3</sub>
218.9856	62	C <sub>4</sub> F <sub>9</sub>	49.9968	1.0	CF <sub>2</sub>
213.9903	0.6	C <sub>4</sub> F <sub>8</sub> N	30.9984	2.3	CF

## COMMON FRAGMENTATION PATTERNS OF FAMILIES OF ORGANIC COMPOUNDS

The following table provides a guide to the identification and interpretation of commonly observed mass spectral fragmentation patterns for common organic functional groups.<sup>1-9</sup> It is, of course, highly desirable to augment mass spectroscopic data with as much other structural information as possible. Especially useful in this regard will be the confirmatory information of infrared and ultraviolet spectrophotometry, as well as nuclear magnetic resonance spectrometry.

### REFERENCES

1. Bowie, J.H., Williams, D.H., Lawesson, S.O., Madsen, J.O., Nolde, C., and Schroll, G., Studies in mass spectrometry. XV. Mass spectra of sulphoxides and sulphones: the formation of C–C and C–O bonds upon electron impact, *Tetrahedron*, 22, 3515, 1966.
2. Johnstone, R.A.W. and Rose, M.E., *Mass Spectrometry for Chemical and Biochemists*, Cambridge University Press, Cambridge, U.K., 1996.
3. Lee, T.A., *A Beginner's Guide to Mass Spectral Interpretation*, Wiley, New York, 1998.
4. McLafferty, F.W., *Interpretation of Mass Spectra*, 4th ed., University Science Books, Mill Valley, CA, 1993.
5. Pasto, D.J. and Johnson, C.R., *Organic Structure Determination*, Prentice Hall, Englewood Cliffs, NJ, 1969.
6. Silverstein, R.M., Bassler, G.C., and Morrill, T.C., *Spectroscopic Identification of Organic Compounds*, 6th ed., John Wiley & Sons, New York, 1998.
7. Smakman, R. and deBoer, T.J., The mass spectra of some aliphatic and alicyclic sulphoxides and sulphones, *Org. Mass Spectrosc.*, 3, 1561, 1970.
8. Smith, R.M., *Understanding Mass Spectra: A Basic Approach*, Wiley, New York, 1999.
9. Watson, T.J. and Watson, J.T., *Introduction to Mass Spectrometry*, Lippincott, Williams & Wilkins, Philadelphia, 1997.

### Common Fragmentation Patterns of Families of Organic Compounds

Family	Molecular Ion Peak	Common Fragments and Characteristic Peaks
Acetals		Cleavage of all C–O, C–H, and C–C bonds around the original aldehydic carbon
Alcohols	Weak for 1 and 2°; not detectable for 3°; strong for benzyl alcohols	Loss of 18 (H <sub>2</sub> O — usually by cyclic mechanism); loss of H <sub>2</sub> O and olefin simultaneously with four (or more) carbon-chain alcohols; prominent peak at m/e = 31 (CH <sub>2</sub> ÖH) <sup>+</sup> for 1° alcohols; prominent peak at m/e = (RCHÖH) <sup>+</sup> for 2° and m/e = (R <sub>2</sub> CÖH) <sup>+</sup> for 3° alcohols
Aldehydes	Low intensity	Loss of aldehydic hydrogen (strong M-1 peak, especially with aromatic aldehydes); strong peak at m/e = 29 (HC=O <sup>+</sup> ); loss of chain attached to alpha carbon (beta cleavage); McLafferty rearrangement via beta cleavage if gamma hydrogen is present
Alkanes		
Chain	Low intensity	Loss of 14 units (CH <sub>2</sub> )
Branched	Low intensity	Cleavage at the point of branch; low intensity ions from random rearrangements
Alicyclic	Rather intense	Loss of 28 units (CH <sub>2</sub> =CH <sub>2</sub> ) and side chains
Alkenes (olefins)	Rather high intensity (loss of $\pi$ -electron) especially in case of cyclic olefins	Loss of units of general formula C <sub>n</sub> H <sub>2n-1</sub> <sup>+</sup> ; formation of fragments of the composition C <sub>n</sub> H <sub>2n</sub> (via McLafferty rearrangement); retro Diels–Alder fragmentation
Alkyl halides	Abundance of molecular ion F < Cl < Br < I; intensity decreases with increase in size and branching	Loss of fragments equal to the mass of the halogen until all halogens are cleaved off
Fluorides	Very low intensity	Loss of 20 (HF); loss of 26 (C <sub>2</sub> H <sub>2</sub> ) in case of fluorobenzenes
Chlorides	Low intensity; characteristic isotope cluster	Loss of 35 (Cl) or 36 (HCl); loss of chain attached to the gamma carbon to the carbon carrying the Cl
Bromides	Low intensity; characteristic isotope cluster	Loss of 79 (Br); loss of chain attached to the gamma carbon to the carbon carrying the Br
Iodides	Higher than other halides	Loss of 127 (I)
Alkynes	Rather high intensity (loss of $\pi$ -electron)	Fragmentation similar to that of alkenes
Amides	Rather high intensity	Strong peak at m/e = 44 indicative of a 1° amide (O=C=NH <sub>2</sub> ) <sup>+</sup> ; base peak at m/e = 59 (CH <sub>2</sub> =C(OH)NH <sub>2</sub> ) <sup>+</sup> ; possibility of McLafferty rearrangement; loss of 42 (C <sub>2</sub> H <sub>2</sub> O) for amides of the form RNHCOCH <sub>3</sub> when R is aromatic ring
Amines	Hardly detectable in case of acyclic aliphatic amines; high intensity for aromatic and cyclic amines	Beta cleavage yielding >C=N <sup>+</sup> ; base peak for all 1° amines at m/e = 30 (CH <sub>2</sub> =NH <sub>2</sub> ) <sup>+</sup> ; moderate M-1 peak for aromatic amines; loss of 27 (HCN) in aromatic amines; fragmentation at alpha carbons in cyclic amines
Aromatic hydrocarbons (arenes)	Rather intense	Loss of side chain; formation of RCH=CHR <sup>+</sup> (via McLafferty rearrangement); cleavage at the bonds beta to the aromatic ring; peaks at m/e = 77 (benzene ring, especially monosubstituted), 91 (tropyllium); the ring position of alkyl substitution has very little effect on the spectrum
Carboxylic acids	Weak for straight-chain monocarboxylic acids; large if aromatic acids	Base peak at m/e = 60 (CH <sub>2</sub> =C(OH) <sub>2</sub> ) if $\delta$ -hydrogen is present; peak at m/e = 45 (COOH); loss of 17 (–OH) in case of aromatic acids or short-chain acids
Disulfides	Rather low intensity	Loss of olefins (m/e equal to R–S–S–H <sup>+</sup> ); strong peak at m/e = 66 (HSSH <sup>+</sup> )
Phenols	Highly intense peak (base peak <sup>a</sup> generally)	Loss of 28 (C=O) and 29 (CHO); strong peak at m/e = 65 (C <sub>5</sub> H <sub>5</sub> <sup>+</sup> )
Sulfides (thioethers)	Rather low intensity peak but higher than that of corresponding ether	Similar to those of ethers (–O– substituted by –S–); aromatic sulfides show strong peaks at m/e = 109 (C <sub>6</sub> H <sub>5</sub> S <sup>+</sup> ), 65 (C <sub>5</sub> H <sub>5</sub> <sup>+</sup> ), 91 (tropyllium ion)
Sulfonamides	Rather intense	Loss of m/e = 64 (SONH <sub>2</sub> ) and m/e = 27 (HCN) in case of benzenesulfonamide



**Common Fragmentation Patterns of Families of Organic Compounds (continued)**

Family	Molecular Ion Peak	Common Fragments and Characteristic Peaks
Esters	Rather weak intensity	Base peak <sup>a</sup> at $m/e$ equal to the mass of $R-C\equiv O^+$ ; peaks at $m/e$ equal to the mass of $^+O=C-OR'$ , the mass of $OR'$ and $R'$ ; McLafferty rearrangement possible in case of (1) presence of a beta hydrogen in $R'$ (peak at $m/e$ equal to the mass of $R-C(^+OH)OH$ , and (2) presence of a gamma hydrogen in $R$ peak at $m/e$ equal to the mass of $(CH_2=C(^+OH)OR)$ ; loss of 42 ( $CH_2=C=O$ ) in case of benzyl esters; loss of $ROH$ via the <i>ortho</i> effect in case of <i>o</i> -substituted benzoates
Ketones	Rather high intensity peak	Loss of $R$ -groups attached to the $>C=O$ (alpha cleavage); peak at $m/e = 43$ for all methyl ketones ( $CH_3CO^+$ ); McLafferty rearrangement via beta cleavage if gamma hydrogen is present; loss of $m/e = 28$ ( $C=O$ ) for cyclic ketones after initial alpha cleavage and McLafferty rearrangement
Mercaptan (thiols)	Rather low intensity but higher than that of corresponding alcohol	Similar to those of alcohols ( $-OH$ substituted by $-SH$ ); loss of $m/e = 45$ ( $CHS$ ) and $m/e = 44$ ( $CS$ ) for aromatic thiols
Nitriles	Unlikely to be detected except in case of acetonitrile ( $CH_3CN$ ) and propionitrile ( $C_2H_5CN$ )	$M + 1$ ion may appear (especially at higher pressures); $M - 1$ peak is weak but detectable ( $R-CH=C=N^+$ ); base peak at $m/e = 41$ ( $CH_2=C=NH$ ); McLafferty rearrangement possible; loss of $HCN$ is case of cyanobenzenes
Nitrites	Absent (or very weak at best)	Base peak at $m/e = 30$ ( $NO^+$ ); large peak at $m/e = 60$ ( $CH_2=ONO$ ) in all unbranched nitrites at the alpha carbon; absence of $m/e = 46$ permits differentiation from nitro compounds
Nitro compounds	Seldom observed	Loss of 30 ( $NO$ ); subsequent loss of $CO$ (in case of aromatic nitro compounds); loss of $NO_2$ from molecular ion peak
Sulfones	High intensity	Similar to sulfoxides; loss of mass equal to $RSO_2$ ; aromatic heterocycles show peaks at $M-32$ (sulfur), $M-48$ ( $SO$ ), $M-64$ ( $SO_2$ )
Sulfoxides	High intensity	Loss of 17 ( $OH$ ); loss of alkene ( $m/e$ equal to $RSOH^+$ ) peak at $m/e = 63$ ( $CH_2=SOH^+$ ); aromatic sulfoxides show peak at $m/e = 125$ ( $^+S-CH=CHCH=CHC=O$ ), 97 ( $C_6H_5S^+$ ), 93 ( $C_6H_5OH$ ); aromatic heterocycles show peaks at $M-16$ (oxygen), $M-29$ ( $COH$ ), $M-48$ ( $SO$ )

<sup>a</sup> The base peak is the most intense peak in the mass spectrum and is often the molecular ion peak,  $M^+$ .

## COMMON FRAGMENTS LOST

The following table gives a list of neutral species that are most commonly lost when measuring the mass spectra of organic compounds. The list is suggestive rather than comprehensive and should be used in conjunction with other sources.<sup>1-4</sup> The listed fragments include only combinations of carbon, hydrogen, oxygen, nitrogen sulfur, and the halogens.

## REFERENCES

1. Hamming, M. and Foster, N., *Interpretation of Mass Spectra of Organic Compounds*, Academic Press, New York, 1972.
2. McLafferty, F.W., *Interpretation of Mass Spectra*, 4th ed., University Science Books, Mill Valley, CA, 1993.
3. Silverstein, R.M., Bassler, G.C., and Morrill, T.C., *Spectroscopic Identification of Organic Compounds*, 6th ed., John Wiley & Sons, New York, 1996.
4. Bruno, T.J., *CRC Handbook for the Analysis and Identification of Alternative Refrigerants*, CRC Press, Boca Raton, FL, 1995.

Common Fragments Lost			
Mass Lost	Fragment Lost	Mass Lost	Fragment Lost
1	H·	51	·CHF <sub>2</sub>
15	CH <sub>3</sub> ·	52	C <sub>4</sub> H <sub>4</sub> ·, C <sub>2</sub> N <sub>2</sub>
17	OH·	54	CH <sub>2</sub> =CHCH=CH <sub>2</sub>
18	H <sub>2</sub> O	55	CH <sub>2</sub> =CH-CH·CH <sub>3</sub>
19	F·	56	CH <sub>2</sub> =CH-CH <sub>2</sub> CH <sub>3</sub> ·; CH <sub>3</sub> CH=CHCH <sub>3</sub> ·; CO (2 mol)
20	HF	57	C <sub>4</sub> H <sub>9</sub> ·
26	HC≡CH·; ·C≡N	58	·NCS; (CH <sub>3</sub> ) <sub>2</sub> C=O·; (NO and CO)
27	CH <sub>2</sub> -CH·; HC≡N	59	CH <sub>3</sub> OC≡O·; CH <sub>3</sub> CONH <sub>2</sub> ·; C <sub>2</sub> H <sub>3</sub> S·
28	CH <sub>2</sub> =CH <sub>2</sub> ·; C=O·; (HCN and H)	60	C <sub>3</sub> H <sub>7</sub> OH
29	CH <sub>3</sub> CH <sub>2</sub> ·; H-C=O	61	CH <sub>3</sub> CH <sub>2</sub> S·; (CH <sub>2</sub> ) <sub>2</sub> S·H
30	·CH <sub>2</sub> NH <sub>2</sub> ·; HCHO·; NO	62	[H <sub>2</sub> S and CH <sub>2</sub> =CH <sub>2</sub> ]
31	CH <sub>3</sub> O·; ·CH <sub>2</sub> OH; CH <sub>3</sub> NH <sub>2</sub>	63	·CH <sub>2</sub> CH <sub>2</sub> Cl
32	CH <sub>3</sub> OH·; S	64	S <sub>2</sub> ·; SO <sub>2</sub> ·; C <sub>5</sub> H <sub>4</sub> ·
33	HS·	68	CH <sub>2</sub> =CHC(CH <sub>3</sub> )=CH <sub>2</sub>
34	H <sub>2</sub> S	69	CF <sub>3</sub> ·; C <sub>5</sub> H <sub>9</sub> ·
35	Cl·	71	C <sub>5</sub> H <sub>11</sub> ·
36	HCl <sub>2</sub> H <sub>2</sub> O	73	CH <sub>3</sub> CH <sub>2</sub> OC=O
37	H <sub>2</sub> Cl	74	C <sub>4</sub> H <sub>9</sub> OH
38	C <sub>3</sub> H <sub>2</sub> ·; C <sub>2</sub> N·; F <sub>2</sub>	75	C <sub>6</sub> H <sub>3</sub>
39	C <sub>3</sub> H <sub>3</sub> ·; HC <sub>2</sub> N	76	C <sub>6</sub> H <sub>4</sub> ·; CS <sub>2</sub>
40	CH <sub>3</sub> C≡CH	77	C <sub>6</sub> H <sub>5</sub> ·; HCS <sub>2</sub>
41	CH <sub>2</sub> =CHCH <sub>2</sub> ·	78	C <sub>6</sub> H <sub>6</sub> ·; H <sub>2</sub> CS <sub>2</sub> ·; C <sub>5</sub> H <sub>4</sub> N
42	CH <sub>2</sub> =CHCH <sub>3</sub> ·; CH <sub>2</sub> =C=O·; (CH <sub>2</sub> ) <sub>3</sub> ·; NCO·; NCNH <sub>2</sub>	79	Br·; C <sub>5</sub> H <sub>5</sub> N
43	C <sub>3</sub> H <sub>7</sub> ·; CH <sub>3</sub> C=O·; CH <sub>2</sub> =CH-O·; HCNO	80	HBr
44	CH <sub>2</sub> =CHOH·; CO <sub>2</sub> ·; N <sub>2</sub> O·; CONH <sub>2</sub> ·; NHCH <sub>2</sub> CH <sub>3</sub>	85	·CClF <sub>2</sub>
45	CH <sub>3</sub> CHOH·; CH <sub>3</sub> CH <sub>2</sub> O·; CO <sub>2</sub> H·; CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub>	100	CF <sub>2</sub> =CF <sub>2</sub>
46	CH <sub>3</sub> CH <sub>2</sub> OH·; NO <sub>2</sub>	119	CF <sub>3</sub> CF <sub>2</sub> ·
47	CH <sub>3</sub> S	122	C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> H
48	CH <sub>3</sub> SH·; SO·; O <sub>3</sub>	127	I·
49	·CH <sub>2</sub> Cl	128	HI

## IMPORTANT PEAKS IN THE MASS SPECTRA OF COMMON SOLVENTS

The following table gives the most important peaks that appear in the mass spectra of the most common solvents, which may be found as impurities in organic samples. The solvents are classified in ascending order, based on their  $M^+$  peaks. The highest intensity peaks are indicated with the parenthetical 100%.<sup>1-4</sup>

## REFERENCES

1. Clere, J.T., Pretsch, E., and Seibl, J., *Studies in Analytical Chemistry. I. Structural Analysis of Organic Compounds by Combined Application of Spectroscopic Methods*, Elsevier, Amsterdam, 1981.
2. McLafferty, F.W., *Interpretation of Mass Spectra*, 4th ed., University Science Books, Mill Valley, CA, 1993.
3. Pasto, D.J. and Johnson, C.R., *Organic Structure Determination*, Prentice Hall, Englewood Cliffs, NJ, 1969.
4. Smith, R.M., *Understanding Mass Spectra: A Basic Approach*, Wiley, New York, 1999.

Solvents	Formula	$M^+$	Important Peaks (m/e)
Water	H <sub>2</sub> O	18 (100%)	17
Methanol	CH <sub>3</sub> OH	32	31 (100%), 29, 15
Acetonitrile	CH <sub>3</sub> CN	41 (100%)	40, 39, 38, 28, 15
Ethanol	CH <sub>3</sub> CH <sub>2</sub> OH	46	45, 31 (100%), 27, 15
Dimethylether	CH <sub>3</sub> OCH <sub>3</sub>	46 (100%)	45, 29, 15
Acetone	CH <sub>3</sub> COCH <sub>3</sub>	58	43 (100%), 42, 39, 27, 15
Acetic acid	CH <sub>3</sub> CO <sub>2</sub> H	60	45, 43, 18, 15
Ethylene glycol	HOCH <sub>2</sub> CH <sub>2</sub> OH	62	43, 33, 31 (100%), 29, 18, 15
Furan	C <sub>4</sub> H <sub>4</sub> O	68 (100%)	42, 39, 38, 31, 29, 18
Tetrahydrofuran	C <sub>4</sub> H <sub>8</sub> O	72	71, 43, 42 (100%), 41, 40, 39, 27, 18, 15
<i>n</i> -Pentane	C <sub>5</sub> H <sub>12</sub>	72	57, 43 (100%), 42, 41, 39, 29, 28, 27, 15
Dimethylformamide (DMF)	HCON(CH <sub>3</sub> ) <sub>2</sub>	73 (100%)	58, 44, 42, 30, 29, 28, 18, 15
Diethylether	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	74	59, 45, 41, 31 (100%), 29, 27, 15
Methylacetate	CH <sub>3</sub> CO <sub>2</sub> CH <sub>3</sub>	74	59, 43 (100%), 42, 32, 29, 28, 15
Carbon disulfide	CS <sub>2</sub>	76 (100%)	64, 44, 32
Benzene	C <sub>6</sub> H <sub>6</sub>	78 (100%)	77, 52, 51, 50, 39, 28
Pyridine	C <sub>5</sub> H <sub>5</sub> N	79 (100%)	80, 78, 53, 52, 51, 50, 39, 26
Dichloromethane	CH <sub>2</sub> Cl <sub>2</sub>	84	86, 51, 49 (100%), 48, 47, 35, 28
Cyclohexane	C <sub>6</sub> H <sub>12</sub>	84	69, 56, 55, 43, 42, 41, 39, 27
<i>n</i> -Hexane	C <sub>6</sub> H <sub>14</sub>	86	85, 71, 69, 57 (100%), 43, 42, 41, 39, 29, 28, 27
1,4-Dioxane	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	88 (100%)	87, 58, 57, 45, 43, 31, 30, 29, 28
Tetramethylsilane (TMS)	(CH <sub>3</sub> ) <sub>4</sub> Si	88	74, 73, 55, 45, 43, 29
1,2-Dimethoxy ethane	(CH <sub>3</sub> OCH <sub>2</sub> ) <sub>2</sub>	90	60, 58, 45 (100%), 31, 29
Toluene	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	92	91 (100%), 65, 51, 39, 28
Chloroform	CHCl <sub>3</sub>	118	120, 83, 81 (100%), 47, 35, 28
Chlorodorm-d <sub>1</sub>	CDCl <sub>3</sub>	119	121, 84, 82 (100%), 48, 47, 35, 28
Carbon tetrachloride	CCl <sub>4</sub>	152 (not seen)	121, 119, 117 (100%), 84, 82, 58.5, 47, 35, 28
Tetrachloroethene	CCl <sub>2</sub> =CCl <sub>2</sub>	164 (not seen)	168, 166 (100%), 165, 164, 131, 129, 128, 94, 82, 69, 59, 47, 31, 24

## REAGENT GASES FOR CHEMICAL IONIZATION MASS SPECTROMETRY

The following tables provide guidance in the selection and optimization of reagents in high-pressure chemical ionization mass spectrometry, as applied with gas chromatography or as a stand-alone technique.<sup>1-3</sup> The first table provides data on positive ion reagent gases, which are called Bronsted acid reagents. Here, we provide the proton affinity (PA) of the conjugate base, the hydride ion affinity (the enthalpy of the reaction of the positive ion with H<sup>-</sup>). The second table provides data on negative ion reagent gases, which are called Bronsted base reagents. Here, we provide the proton affinity of the negative ion and the electron affinity of the base.

### REFERENCES

1. Harrison, A.G., *Chemical Ionization Mass Spectrometry*, CRC Press, Boca Raton, FL, 1992.
2. Message, G.M., *Practical Aspects of Gas Chromatography/Mass Spectrometry*, John Wiley & Sons (Wiley Interscience), New York, 1984.
3. Karasek, F.W. and Clement, R.E., *Basic Gas Chromatography-Mass Spectrometry*, Elsevier, Amsterdam, 1988.

Positive Ion Reagent Gases for Chemical Ionization Mass Spectrometry

Reagent Gas	Reactant Ion(s)	PA, kJ/mol	PA, kcal/mol	HIA, kJ/mol	HIA, kcal/mol	Comments
H <sub>2</sub>	H <sub>3</sub> <sup>+</sup>	423.7	101.2	1260	300	General-purpose reagent gas
N <sub>2</sub> + H <sub>2</sub>	N <sub>2</sub> H <sup>+</sup>	494.9	118.2	1180	282	
CO <sub>2</sub> + H <sub>2</sub>	CO <sub>2</sub> H <sup>+</sup>	547.6	130.8	1130	270	
N <sub>2</sub> O + H <sub>2</sub>	N <sub>2</sub> OH <sup>+</sup>	581.1	138.8	1090	261	
CO + H <sub>2</sub>	HCO <sup>+</sup>	596.2	142.4	1080	258	
CH <sub>4</sub>	CH <sub>5</sub> <sup>+</sup>	551.0	131.6	1130	269	Most widely used reagent gas; usually used initially for most work; degree of fragmentation is relatively large; background spectrum is often large; can produce a large number of additional ions and quasi-molecular ions
	C <sub>2</sub> H <sub>5</sub> <sup>+</sup>	680.8	162.6	1130	271	
H <sub>2</sub> O	H <sup>+</sup> (H <sub>2</sub> O) <sub>x</sub> x is pressure dependent	697.1	166.5	980	234	Used for alcohols, ketones, esters, and amines
CH <sub>3</sub> OH	H <sup>+</sup> (CH <sub>3</sub> OH) <sub>x</sub> x is pressure dependent	761.6	181.9	917	219	
C <sub>3</sub> H <sub>8</sub>	C <sub>3</sub> H <sub>7</sub> <sup>+</sup>	751.5	179.5	1050	250	Uncommon reagent gas
<i>i</i> -C <sub>4</sub> H <sub>10</sub>	C <sub>4</sub> H <sub>9</sub> <sup>+</sup>	820.2	195.9	976	233	General-purpose reagent gas; fragmentation pattern is similar to that produced by ammonia
NH <sub>3</sub>	H <sup>+</sup> (NH <sub>3</sub> ) <sub>x</sub> x is pressure dependent	854.1	204.0	825	197	

### Negative Ion Reagent Gases for Chemical Ionization Mass Spectrometry

Reagent Gas	Reactant Ion(s)	PA, kJ/mol	PA, kcal/mol	HIA, kJ/mol	HIA, kcal/mol	Comments
H <sub>2</sub>	H <sup>-</sup>	1675	400	72.9	17.4	H <sup>-</sup> ion is difficult to form in good yields; sometimes used for analysis of alcohols
NH <sub>3</sub>	NH <sub>2</sub> <sup>-</sup>	1691	404	75.4	18.0	General-purpose gas, used for the analysis of esters
N <sub>2</sub> O	OH <sup>-</sup>	1637	391	177	42.2	Most common negative ion reagent gas used; often used as a mixture with N <sub>2</sub> O to eliminate O <sup>-</sup> signal; sometimes used as a N <sub>2</sub> O/He/N <sub>2</sub> O, 1:1:1 mixture; used with CH <sub>4</sub> for simultaneous +/- ion work
CH <sub>3</sub> NO <sub>2</sub>	CH <sub>3</sub> O <sup>-</sup>	1595	381	152	36.2	Almost as strong a base as OH <sup>-</sup> ; used as a 1% mixture in CH <sub>4</sub>
O <sub>2</sub>	O <sub>2</sub> <sup>-</sup>	1478	353	42.3	10.1	Used in the analysis of alcohols
C <sub>2</sub> Cl <sub>3</sub> F <sub>3</sub> (R-113)	Cl <sup>-</sup>	1394	333	349	83.4	Cl <sup>-</sup> is a weak Bronsted base useful for acidic compounds
CH <sub>2</sub> Br <sub>2</sub>	Br <sup>-</sup>	1357	324	325	77.6	Br <sup>-</sup> is a weak Bronsted base (weaker than Cl <sup>-</sup> ) that reacts with analytes that have a moderately acidic hydrogen

## PROTON AFFINITIES OF SOME SIMPLE MOLECULES

The following table gives the proton affinities (PA) of some simple molecules. For the occurrence of proton transfer (or reaction) between a reactant ion and a sample molecule, the reaction must be exothermic. Thus,

$$\Delta H (\text{reaction}) = \text{PA (reactant gas)} - \text{PA (sample)} < 0$$

The more exothermic the reaction, the greater the degree of fragmentation. Endothermic reactions do not yield a protonated form of a sample; therefore, the sample compound cannot be recorded. One can choose the proper reactant gas that will give the correct fragmentation pattern of a desired compound out of a mixture of compounds.<sup>1-3</sup> Chapman<sup>3</sup> lists positive ion chemical ionization applications by reagent gas and by compounds analyzed. The values are provided in kcal/mol for convenience; to convert to the appropriate SI unit (kJ/mol), multiply by 4.1845.

## REFERENCES

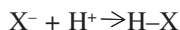
1. Field, F.H., Chemical ionization mass spectrometry, *Acc. Chem. Res.*, 1, 42, 1968.
2. Harrison, A.G., *Chemical Ionization Mass Spectrometry*, 2nd ed., CRC Press, Boca Raton, FL, 1992.
3. Chapman, J.R., *Practical Organic Mass Spectrometry*, 2nd ed., John Wiley & Sons, Chichester, U.K., 1995.

Proton Affinities of Some Simple Molecules

Family	Typical Examples (PA in kcal/mol)
Alcohols	CH <sub>3</sub> OH (184.9); CH <sub>3</sub> CH <sub>2</sub> OH (190.3); CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH (191.4); (CH <sub>3</sub> ) <sub>3</sub> COH (195.0); CF <sub>3</sub> CH <sub>2</sub> OH (174.9)
Aldehydes	HCHO (177.2); CH <sub>3</sub> CHO (188.9); CH <sub>3</sub> CH <sub>2</sub> CHO (191.4); CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CHO (193.3)
Alkanes	CH <sub>4</sub> (130.5); (CH <sub>3</sub> ) <sub>3</sub> CH (195)
Alkenes	H <sub>2</sub> C=CH <sub>2</sub> (163.5); CH <sub>3</sub> CH=CH <sub>2</sub> (184.9); (CH <sub>3</sub> ) <sub>2</sub> C=CH <sub>2</sub> (196.9); <i>trans</i> -CH <sub>3</sub> CH=CHCH <sub>3</sub> (182.0)
Aromatics, substituted C <sub>6</sub> H <sub>5</sub> -G	G=H (182.8); -Cl (181.7); -F (181.5); -CH <sub>3</sub> (191.2); -C <sub>2</sub> H <sub>5</sub> (192.2); -CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> (191.0); -CH(CH <sub>3</sub> ) <sub>2</sub> (191.4); -C(CH <sub>3</sub> ) <sub>3</sub> (191.6); -NO <sub>2</sub> (193.8); -OH (196.2); -CN (196.3); -CHO (200.3); -OCH <sub>3</sub> (200.6); -NH <sub>2</sub> (211.5)
Amines	1°: NH <sub>3</sub> (205.0); CH <sub>3</sub> NH <sub>2</sub> (214.1); C <sub>2</sub> H <sub>5</sub> NH <sub>2</sub> (217.1); CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> (218.5); CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> (219.0) 2°: (CH <sub>3</sub> ) <sub>2</sub> NH (220.5); (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NH (225.1); (CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> NH (227.4) 3°: (CH <sub>3</sub> ) <sub>3</sub> N (224.3); (C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N (231.2); (CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub> N (233.4)
Carboxylic acids	HCO <sub>2</sub> H (182.8); CH <sub>3</sub> CO <sub>2</sub> H (190.7); CH <sub>3</sub> CH <sub>2</sub> CO <sub>2</sub> H (193.4); CF <sub>3</sub> CO <sub>2</sub> H (176.0)
Dienes	CH <sub>2</sub> =CHCH=CH <sub>2</sub> (193); E-CH <sub>2</sub> =CHCH=CHCH <sub>3</sub> (201.8); E-CH <sub>2</sub> =CHC(CH <sub>3</sub> )=CHCH <sub>3</sub> (205.7); cyclopentadiene (200.0)
Esters	HCO <sub>2</sub> CH <sub>3</sub> (190.4); HCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> (194.2); HCO <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> (195.2); CH <sub>3</sub> CO <sub>2</sub> CH <sub>3</sub> (198.3); CH <sub>3</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> (201.3); CH <sub>3</sub> CO <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> (202.0)
Ethers	(CH <sub>3</sub> ) <sub>2</sub> O (193.1); (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O (200.4); (CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> O (202.9); (CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> O (203.9); tetrahydrofuran (199.6); tetrahydropyran (200.7)
Ketones	CH <sub>3</sub> COCH <sub>3</sub> (197.2); CH <sub>3</sub> COC <sub>2</sub> H <sub>5</sub> (199.4)
Nitriles (cyano compounds)	HCN (178.9); CH <sub>3</sub> CN (190.9); C <sub>2</sub> H <sub>5</sub> CN (192.8); CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CN (193.8)
Sulfides	(CH <sub>3</sub> ) <sub>2</sub> S (200.7); (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> S (205.6); [(CH <sub>3</sub> ) <sub>2</sub> CH] <sub>2</sub> S (209.3)
Thiols	H <sub>2</sub> S (176.6); CH <sub>3</sub> SH (188.6); C <sub>2</sub> H <sub>5</sub> SH (192.0); [(CH <sub>3</sub> ) <sub>2</sub> CH] <sub>2</sub> SH (194.7)

## PROTON AFFINITIES OF SOME ANIONS

The following table lists the proton affinities of some common anions ( $X^-$ ). Since the reaction of an anion ( $X^-$ ) with a proton ( $H^+$ ),



is exothermic, it can be used to generate other anions that possess a smaller proton affinity value by the addition of the corresponding neutral species.<sup>1,2</sup>

## REFERENCES

1. Chapman, J.R., *Practical Organic Mass Spectrometry*, 2nd ed., John Wiley & Sons, Chichester, U.K., 1995.
2. Harrison, A.G., *Chemical Ionization Mass Spectrometry*, 2nd ed., CRC Press, Boca Raton, FL, 1992.

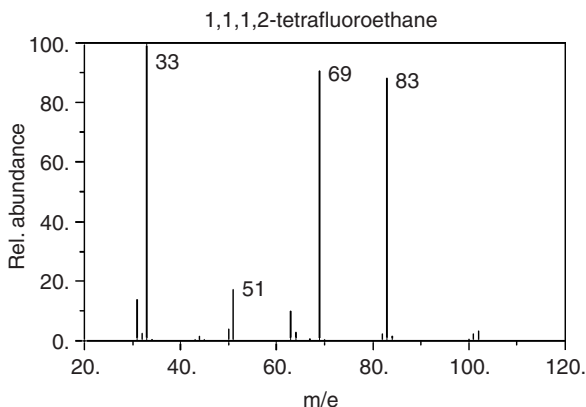
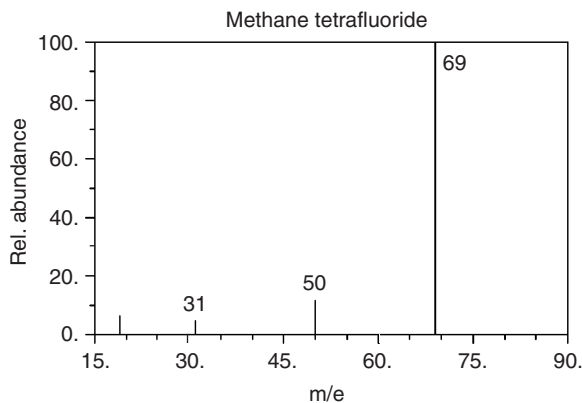
Proton Affinities of Some Anions	
Anion	Proton Affinity (kJ/mol)
$NH_2^-$	1689
$H^-$	1676
$OH^-$	1636
$O^-$	1595
$CH_3O^-$	1583
$(CH_3)_2CHO^-$	1565
$^-CH_2CN$	1556
$F^-$	1554
$C_5H_5^-$	1480
$O_2^-$	1465
$CN^-$	1462
$Cl^-$	1395

## DETECTION OF LEAKS IN MASS SPECTROMETER SYSTEMS

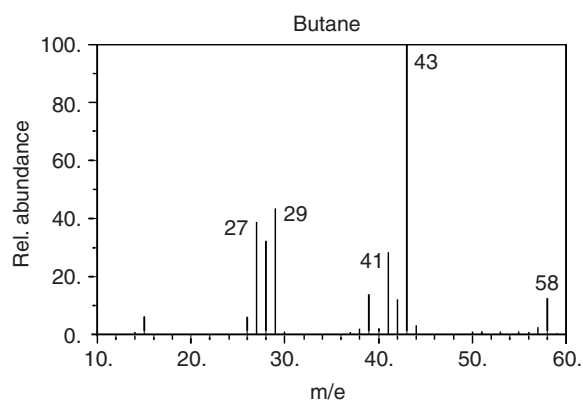
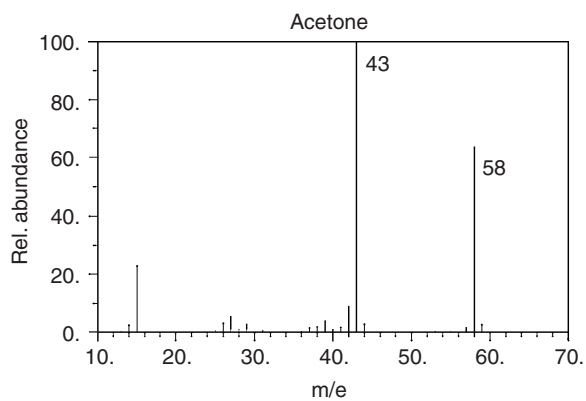
The following tables provide guidance for troubleshooting possible leaks in the vacuum systems of mass spectrometers, especially those operating in electron impact mode. Leak testing is commonly done by playing a stream of a pure gas against a fitting, joint, or component that is suspected of being a leak source. If in fact the component is the source of a leak, one should be able to note the presence of the leak detection fluid on the mass spectrum. Here we present the mass spectra of methane tetrafluoride, 1,1,1,2-tetrafluoroethane (R-134a), *n*-butane, and acetone.<sup>1,2</sup> Methane tetrafluoride, 1,1,1,2-tetrafluoroethane, and *n*-butane are handled as gases, while acetone is handled as a liquid. Typically, *n*-butane is dispensed from a disposable lighter, and acetone is dispensed from a dropper. Care must be taken when using acetone or a butane lighter for leak checking because of the flammability of these fluids.

## REFERENCES

1. Bruno, T.J., *CRC Handbook for the Analysis and Identification of Alternative Refrigerants*, CRC Press, Boca Raton, FL, 1994.
2. *NIST Chemistry Web Book*, NIST Standard Reference Database 69, March 2003 release.







## MASS RESOLUTION REQUIRED TO RESOLVE COMMON SPECTRAL INTERFERENCES ENCOUNTERED IN INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

The table below lists some common spectral interferences that are encountered in inductively coupled plasma mass spectrometry (ICP-MS), as well as the resolution that is necessary to analyze them.<sup>1</sup> The resolution is presented as a dimensionless ratio. As an example, the relative molecular mass (RMM) of the polyatomic ion  $^{15}\text{N}^{16}\text{O}^+$  would be  $15.000108 + 15.994915 = 30.995023$ . This would interfere with  $^{31}\text{P}^+$  at a mass of 30.973762. The required resolution would be  $\text{RMM}/\delta\text{RMM}$ , or  $30.973762/0.021261 = 1457$ . One should bear in mind that as resolution increases, the sensitivity decreases with subsequent effects on the price of the instrument. Note that small differences exist in the published exact masses of isotopes, but for the calculation of the required resolution, these differences are trivial. Moreover, recent instrumentation has provided rapid, high-resolution mass spectra with an uncertainty of less than 0.01%.

### REFERENCES

1. Gregoire, D.C., Analysis of geological materials by inductively coupled plasma mass spectrometry, *Spectrometry*, 14, 14, 1999.

**Mass Resolution Required to Resolve Common Spectral Interferences  
Encountered in Inductively Coupled Plasma Mass Spectrometry**

Polyatomic Ion	Interfered Isotope (Natural Abundance %)	Required Resolution
$^{14}\text{N}_2^+$	$^{14}\text{Si}^+$ (92.21)	958
$^{15}\text{N}^{16}\text{O}^+$	$^{31}\text{P}^+$ (100)	1457
$^{40}\text{Ar}^{12}\text{O}^+$	$^{52}\text{Cr}^+$ (83.76)	2375
$^{32}\text{S}^{16}\text{O}^+$	$^{48}\text{Tl}^+$ (73.94)	2519
$^{35}\text{Cl}^{16}\text{O}^+$	$^{51}\text{V}^+$ (99.76)	2572
$^{40}\text{Ar}^{35}\text{Cl}^+$	$^{75}\text{As}^+$ (100)	7775
$^{40}\text{Ar}_2^+$	$^{80}\text{Se}^+$ (49.82)	9688

# Atomic Absorption Spectrometry

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## INTRODUCTION FOR ATOMIC SPECTROMETRIC TABLES

The tables presented in this section are designed to aid in the area of atomic spectrometric methods of analysis. The following conventions for abbreviation are recommended by the International Union of Pure and Applied Chemistry:<sup>1</sup>

Atomic emission spectrometry AES  
Atomic absorption spectrometry AAS  
Flame atomic emission spectrometry FAES  
Flame atomic absorption spectrometry FAAS  
Electrothermal atomic absorption spectrometry EAAS  
Inductively coupled plasma atomic emission spectrometry ICP-AES

Other variations such as cold vapor and hydride generation are not abbreviated but spelled out, e.g., cold vapor AAS, hydride generation FAAS, etc. These abbreviations are used whenever appropriate throughout the section.

Several of these tables have appeared in Parsons et al.'s *Handbook*<sup>2</sup> in one form or another. They have been updated to the extent possible, and the wavelength values have been made to conform to those in the National Standard Reference Data System–National Bureau of Standards (NSRDS-NBS) 68<sup>3</sup> wherever possible.

As several of the tables cite the same references, all cited references will be listed at the end of this introduction instead of being repeated at the end of each table. These tables were originally prepared by Parsons et al. for the first edition of this book.<sup>18</sup>

## REFERENCES

1. Commission on spectrochemical and other optical procedures for analysis, nomenclature, symbols, units and their usage in spectrochemical analysis. I. General atomic emission spectroscopy. II. Data interpretation. III. Analytical flame spectroscopy and associated procedures, *Spectrochim. Acta*, 33B, 219, 1978.
2. Parsons, M.L., Smith, B.W., and Bentley, G.E., *Handbook of Flame Spectroscopy*, Plenum Press, New York, 1975.
3. Reader, J., Corliss, C.H., Weise, W.L., and Martin, G.A., *Wavelengths and Transition Probabilities for Atoms and Atomic Ions*, NSRDS-NBS 68, U.S. Government Printing Office, Washington, D.C., 1980.
4. Smith, B.W. and Parsons, M.L., Preparation of standard solutions: critically selected compounds, *J. Chem. Educ.*, 50, 679, 1973.
5. Dean, J.A. and Rains, T.C., Standard solutions for flame spectrometry, in *Flame Emission and Atomic Absorption Spectrometry*, Vol. 2, Marcel Dekker, New York, 1971, p. 327.
6. Thermo Jarrell Ash Corp., *Guide to Analytical Values for TJA Spectrometers*, Thermo Jarrell Ash Corp., Waltham, MA, 1987.
7. Anderson, T.A. and Parsons, M.L., ICP emission spectra III: the spectra for the group IIIA elements and spectral interferences due to group IIA and IIIA elements, *Appl. Spectrosc.*, 38, 625, 1984; Parsons, M.L., Forster, A., and Anderson, D., *An Atlas of Spectral Interferences in ICP Spectroscopy*, Plenum Press, New York, 1980.
8. Park, D.A., Further Investigations of Spectra and Spectral Interferences Due to Group A Elements in ICP Spectroscopy: Groups IVA and VA, Ph.D. thesis, Arizona State University, Tempe; Parsons, M.L., Unpublished data, Los Alamos National Laboratory, Los Alamos, NM, 1987.
9. Perkin-Elmer Corp., *Mercury/Hydride System*, Report 1876/6.79, Norwalk, CT, 1987.
10. Lovett, R.J., Welch, D.L., and Parsons, M.L., On the importance of spectral interferences in atomic absorption spectroscopy, *Appl. Spectrosc.*, 29, 470, 1975.
11. Layman, L., Palmer, B., and Parsons, M.L., Unpublished data taken with the Los Alamos National Laboratory FTS Facility, Los Alamos, NM, 1987.

12. Sneddon, J., Background correction techniques in atomic spectroscopy, *Spectroscopy*, 2, 38, 1987.
13. Wittenberg, G.K., Haun, D.V., and Parsons, M.L., The use of free-energy minimization for calculating beta factors and equilibrium compositions in flame spectroscopy, *Appl. Spectrosc.*, 33, 626, 1979.
14. Parsons, M.L., Smith, B.W., and McElfresh, P.M., On the selection of analysis lines in atomic absorption spectrometry, *Appl. Spectrosc.*, 27, 471, 1973.
15. Parker, L.R., Jr., Morgan, S.L., and Deming, S.N., Simplex optimization of experimental factors in atomic absorption spectrometry, *Appl. Spectrosc.*, 29, 429, 1975.
16. Parsons, M.L. and Winefordner, J.D., Optimization of the critical instrumental parameters for achieving maximum sensitivity and precision in flame-spectrometric methods of analysis, *Appl. Spectrosc.*, 21, 368, 1967.
17. Wiese, W.L., Smith, M.W., and Glennon, B.M., *Atomic Transition Probabilities*, Vol. I, *Hydrogen through Neon*, NSRDS-NBS 4, U.S. Government Printing Office, Washington, D.C., 1966.
18. Bruno, T.J. and Svoronos, P.D.N., *CRC Handbook of Basic Tables for Chemical Analysis*, CRC Press, Boca Raton, FL 1989.

## STANDARD SOLUTIONS: SELECTED COMPOUNDS AND PROCEDURES

The compounds selected for this table were chosen using a rather stringent set of criteria, including stability, purity, ease of preparation, availability, high molecular mass, and toxicity. It is very important to have a compound that is pure and can be dried, weighed, and dissolved with comparative ease. The list of compounds provided here meets those goals as much as possible. No attempt was made to include all compounds that meet these criteria, nor are the compounds in this list trivial to dissolve; some require a rather long time and vigorous conditions.

In this table the significant figures in all columns represent the accuracy with which the atomic masses of the elements are known.

This table was compiled from References 4 and 5.

Standard Solutions: Selected Compounds and Procedures

Element	Compound	Relative Formula Mass	Weight for 1000 µg/l (PPM)-g/l	Solvent	Note
Aluminum	Al-metal	26.982	1.0000	Hot dil. HCl-2 M	APS
Antimony	KSbOC <sub>4</sub> H <sub>4</sub> O <sub>6</sub> · 1/2 H <sub>2</sub> O	324.92	2.6687 (antimony potassium tartarate)	Water	d
	Sb-metal	121.75	1.0000	Hot aq. reg.	
Arsenic	As <sub>2</sub> O <sub>3</sub>	197.84	1.3203	1:1 NH <sub>3</sub>	PS, <sup>a</sup> NIST
Barium	BaCO <sub>3</sub>	197.35	1.4369	Dil. HCl	f
	BaCl <sub>2</sub>	208.25	1.5163	Water	d
Beryllium	Be-metal	9.0122	1.0000	HCl	a
	BeSO <sub>4</sub> ·4H <sub>2</sub> O	177.135	19.6550	Water + acid	g
Bismuth	Bi <sub>2</sub> O <sub>3</sub>	465.96	1.1148	HNO <sub>3</sub>	
	Bi-metal	208.980	1.00000	HNO <sub>3</sub>	
Boron	H <sub>3</sub> BO <sub>3</sub>	61.84	5.720	Water	PS, NIST <sup>k</sup>
Bromine	KBr	119.01	1.4894	Water	APS
Cadmium	CdO	128.40	1.1423	HNO <sub>3</sub>	
	Cd-metal	112.40	1.0000	Dil. HCl	
Calcium	CaCO <sub>3</sub>	100.09	2.4972	Dil. HCl	f
Cerium	(NH <sub>4</sub> ) <sub>2</sub> Ce(NO <sub>3</sub> ) <sub>4</sub>	548.23	3.9126	Water	
Cesium	Cs <sub>2</sub> SO <sub>4</sub>	361.87	1.3614	Water	
Chlorine	NaCl	58.442	1.6485	Water	PS
Chromium	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	294.19	2.8290	Water	PS, NIST
	Cr-metal	51.996	1.0000	HCl	
Cobalt	Co-metal	58.933	1.0000	HNO <sub>3</sub>	APS
Copper	Cu-metal	63.546	1.0000	Dil. HNO <sub>3</sub>	APS
	CuO	69.545	1.2517	Hot HCl	APS
	CuSO <sub>4</sub> ·5H <sub>2</sub> O	249.678	3.92909	Water	
Dysprosium	Dy <sub>2</sub> O <sub>3</sub>	373.00	1.477	Hot HCl	c
Erbium	Er <sub>2</sub> O <sub>3</sub>	382.56	1.1435	Hot HCl	c
Europium	Eu <sub>2</sub> O <sub>3</sub>	351.92	1.1579	Hot HCl	c
Fluorine	NaF	41.988	2.2101	Water	h
Gadolinium	Gd <sub>2</sub> O <sub>3</sub>	362.50	1.1526	Hot HCl	c
Gallium	Ga-metal	69.72	1.000	Hot HNO <sub>3</sub>	i
Germanium	GeO <sub>2</sub>	104.60	1.4410	Hot 1 M NaOH or 50 g oxalic acid + water	
Gold	Au-metal	196.97	1.0000	Hot aq. reg.	APS, NIST
Hafnium	Hf-metal	178.49	1.0000	Hf, Fusion	j
Holmium	Ho <sub>2</sub> O <sub>3</sub>	377.86	1.1455	Hot HCl	c
Indium	In <sub>2</sub> O <sub>3</sub>	277.64	1.2090	Hot HCl	
	In-metal	114.82	1.0000	Dil. HCl	
Iodine	KIO <sub>3</sub>	214.00	1.6863	Water	PS
Iridium	Na <sub>3</sub> IrCl <sub>6</sub>	473.8	2.466	Water	
Iron	Fe-metal	55.847	1.0000	Hot HCl	APS

**Standard Solutions: Selected Compounds and Procedures (continued)**

Element	Compound	Relative Formula Mass	Weight for 1000 µg/l (PPM)-g/l	Solvent	Note
Lanthanum	La <sub>2</sub> O <sub>3</sub>	325.82	1.1728	Hot HCl	c
Lead	Pb(NO <sub>3</sub> ) <sub>2</sub>	331.20	1.5985	HCl	APS, NIST
Lithium	Li <sub>2</sub> CO <sub>3</sub>	73.890	5.3243	Dil. HCl	APS <sup>f</sup>
Lutetium	Lu <sub>2</sub> O <sub>3</sub>	397.94	1.1372	Hot HCl	c
Magnesium	MgO	40.311	1.6581	HCl	
	Mg-metal	24.312	1.0000	Dil. HCl	
Manganese	MnSO <sub>4</sub> ·H <sub>2</sub> O	169.01	3.0764	Water	m
Mercury	HgCl <sub>2</sub>	271.50	1.3535	Water	a
	Hg-metal	200.59	1.0000	5 M HNO <sub>3</sub>	
Molybdenum	MoO <sub>3</sub>	143.94	1.5003	1 M NaOH or 2 M HN <sub>3</sub>	
Neodymium	Nd <sub>2</sub> O <sub>3</sub>	336.48	1.1664	HCl	c
Nickel	Ni-metal	58.71	1.000	Hot HNO <sub>3</sub>	APS
Niobium	Nb <sub>2</sub> O <sub>5</sub>	265.81	1.4305	HF, fusion	m, o
	Nb-metal	92.906	1.0000	HF + H <sub>2</sub> SO <sub>4</sub>	o
Osmium	Os-metal	190.20	1.0000	Hot H <sub>2</sub> SO <sub>4</sub>	b
Palladium	Pd-metal	106.40	1.0000	Hot HNO <sub>3</sub>	
Phosphorus	KH <sub>2</sub> PO <sub>4</sub>	136.09	4.3937	Water	
	(NH <sub>3</sub> ) <sub>2</sub> HPO <sub>4</sub>	209.997	6.77983	Water	
Platinum	K <sub>2</sub> PtCl <sub>4</sub>	415.12	2.1278	Water	APS, NIST
	Pt-metal	195.05	1.0000	Hot aq. reg.	
Potassium	KCl	74.555	1.9067	Water	PS, NIST
	KHC <sub>6</sub> H <sub>4</sub> O <sub>4</sub>	204.22	5.2228	Water	PS, NIST
	(potassium hydrogen phthalate)				
	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	294.19	3.7618	Water	PS, NIST
Praseodymium	Pr <sub>6</sub> O <sub>11</sub>	1021.43	1.20816	HCl	c
Rhenium	Re-metal	186.2	1.000	HNO <sub>3</sub>	
	KReO <sub>4</sub>	289.3	1.554	Water	
Rhodium	Rh-metal	102.91	1.0000	Hot H <sub>2</sub> SO <sub>4</sub>	
Rubidium	Rb <sub>2</sub> SO <sub>4</sub>	267.00	1.5628	Water	
Ruthenium	RuO <sub>4</sub>	165.07	1.6332	Water	
Samarium	Sm <sub>2</sub> O <sub>3</sub>	348.70	2.3193	Hot HCl	c
Scandium	Sc <sub>2</sub> O <sub>3</sub>	137.91	1.5339	Hot HCl	
Selenium	Se-metal	78.96	1.000	Hot HNO <sub>3</sub>	
	SeO <sub>2</sub>	110.9	1.405	Water	
Silicon	Si-metal	28.086	1.0000	NaOH, conc.	
	SiO <sub>2</sub>	60.085	2.1393	HF	
Silver	AgNO <sub>3</sub>	169.875	1.57481	Water	APS <sup>p</sup>
	Ag-metal	107.870	1.0000	HNO <sub>3</sub>	
Sodium	NaCl	58.442	2.5428	Water	PS
	Na <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	134.000	2.91432	Water	PS, NIST
	(sodium oxalate)				
Strontium	SrCO <sub>3</sub>	147.63	1.6849	Dil. HCl	APS <sup>f</sup>
Sulfur	K <sub>2</sub> SO <sub>4</sub>	174.27	5.4351	Water	
	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	114.10	3.5585	Water	
Tantalum	Ta <sub>2</sub> O <sub>5</sub>	441.893	1.22130	HF, fusion	n, o
	Ta-metal	180.948	1.0000	HF + H <sub>2</sub> SO <sub>4</sub>	o
Tellurium	TeO <sub>2</sub>	159.60	1.2507	HCl	
Terbium	Tb <sub>2</sub> O <sub>3</sub>	365.85	1.1512	Hot HCl	c
Thallium	Tl <sub>2</sub> CO <sub>3</sub>	468.75	1.1468	Water	APS <sup>a</sup>
	TlNO <sub>3</sub>	266.37	1.3034	Water	
Thorium	Th(NO <sub>3</sub> ) <sub>4</sub> ·4H <sub>2</sub> O	552.118	2.37943	HNO <sub>3</sub>	
Thulium	Tm <sub>2</sub> O <sub>3</sub>	385.87	1.1421	Hot HCl	c
Tin	Sn-metal	118.69	1.0000	HCl	
	SnO	134.69	1.1348	HCl	
Titanium	Ti-metal	47.90	1.000	1:1 H <sub>2</sub> SO <sub>4</sub>	APS

**Standard Solutions: Selected Compounds and Procedures (continued)**

Element	Compound	Relative Formula Mass	Weight for 1000 µg/l (PPM)-g/l	Solvent	Note
Tungsten	Na <sub>2</sub> WO <sub>4</sub> ·2H <sub>2</sub> O	329.86	1.7942	Water	q
	Na <sub>2</sub> WO <sub>4</sub>	293.83	1.5982	Water	d
Uranium	UO <sub>2</sub>	270.03	1.1344	HNO <sub>3</sub>	PS, NIST
	U <sub>3</sub> O <sub>8</sub>	842.09	1.1792	HNO <sub>3</sub>	
	UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	502.13	2.1095	Water	
Vanadium	V <sub>2</sub> O <sub>5</sub>	181.88	1.78521	Hot HCl	
	NH <sub>4</sub> VO <sub>3</sub>	116.98	2.2963	Dil. HNO <sub>3</sub>	
Ytterbium	Yb <sub>2</sub> O <sub>3</sub>	394.08	1.1386	Hot HCl	c
Yttrium	Y <sub>2</sub> O <sub>3</sub>	225.81	1.2700	Hot HCl	c
Zinc	ZnO	81.37	1.245	HCl	APS
	Zn-metal	65.37	1.000	HCl	APS, NIST
Zirconium	Zr-metal	91.22	1.000	HF, fusion	j
	ZrOCl <sub>2</sub> ·8H <sub>2</sub> O	322.2	3.533	HCl	

*Note:* PS = primary standard; APS = compounds that approach primary standard quality; NIST = compounds sold as primary standards by the NIST Standard Reference Materials Program, 100 Bureau Drive, Gaithersburg, MD 20899-3460 ([www.nist.gov](http://www.nist.gov)).

<sup>a</sup> Highly toxic.

<sup>b</sup> Very highly toxic.

<sup>c</sup> The rare earth oxides, because they absorb CO<sub>2</sub> and water vapor from the atmosphere, should be freshly ignited prior to weighing.

<sup>d</sup> Loses water at 110°C. Water is only slowly regained, but rapid weighing and desiccator storage are required.

<sup>e</sup> Drying at 250°C, rapid weighing, and desiccator storage are required.

<sup>f</sup> Add a quantity of water, then add dilute acid and swirl until the CO<sub>2</sub> has ceased to bubble out, and then dilute.

<sup>g</sup> Dissolve in water, then add 5 ml of concentrated HCl and dilute.

<sup>h</sup> Sodium fluoride solutions will etch glass and should be freshly prepared.

<sup>i</sup> Because the melting point is 29.6°C, the metal may be warmed and weighed as a liquid.

<sup>j</sup> Zr and Hf compounds were not investigated in the laboratory of reference 5.

<sup>k</sup> Boric acid may be weighed directly from the bottle. It loses 1 H<sub>2</sub>O at 100°C, but it is difficult to dry to a constant mass.

<sup>l</sup> Several references suggest that the addition of acid will help stabilize the solution.

<sup>m</sup> This compound may be dried at 100°C without losing the water of hydration.

<sup>n</sup> Nb and Ta are slowly soluble in 40% HF. The addition of H<sub>2</sub>SO<sub>4</sub> accelerates the dissolution process.

<sup>o</sup> Dissolve in 20 ml of hot HF in a platinum dish, add 40 ml of H<sub>2</sub>SO<sub>4</sub> and evaporate to fumes, and dilute with 8 M H<sub>2</sub>SO<sub>4</sub>.

<sup>p</sup> When kept dry, silver nitrate crystals are not affected by light. Solutions should be stored in brown bottles.

<sup>q</sup> Sodium tungstate loses both water molecules at 110°C. The water is not rapidly regained, but the compound should be kept in a desiccator after drying and should be weighed quickly once it is removed.



## **LIMITS OF DETECTION TABLES FOR COMMON ANALYTICAL TRANSITIONS IN AES AND AAS**

The following five tables present the common transitions for analysis and the detection limits for AES and AAS on the basis of source, where appropriate for the specific atom cell indicated. The detection limits are from the literature cited and are given in parts per billion (ppb) or nanograms per milliliter of aqueous solution. The limits of detection (LODs) are generally defined as a signal to noise of two or three. This generally relates to a concentration that produces a signal of two or three times the standard deviation of the measurement. These are measured in dilute aqueous solution and represent the best that the system was capable of measuring. In most cases, the detection limit in real samples will be one or two orders of magnitude higher, or worse, than those stated here. The type designation is I for free atom and II for single ion. In all cases, NO means that no observation was made for the situation indicated, and NA means that either AES or AAS was observed but no detection limit was reported.

In all cases where possible, the wavelengths of the transitions were made to conform with Reference 3; any wavelength below 200 nm is the wavelength given in vacuum; all others are in air.

Limits of Detection for the Air–Hydrocarbon Flame<sup>a</sup>

Element	Symbol	Wavelength (nm)	Type	LOD-AAS (ppb)
Antimony	Sb	217.581	I	100
		231.147	I	100
Bismuth	Bi	223.061	I	50
Calcium	Ca	22.673	I	2
Cesium	Cs	455.5276	I	600
		852.1122	I	50
Chromium	Cr	357.869	I	5
Cobalt	Co	240.725	I	5
Copper	Cu	324.754	I	50
		327.396	I	50
Gallium	Ga	287.424	I	70
Gold	Au	242.795	I	20
Indium	In	303.936	I	50
Iridium	Ir	208.882	I	15,000
		2639.71	I	2000
Iron	Fe	248.3271	I	5
Lead	Pb	283.3053	I	10
Lithium	Li	670.776	I	5
Magnesium	Mg	285.213	I	0.3
Manganese	Mn	279.482	I	2
		403.076	I	2
Mercury	Hg	253.652	I	500
Molybdenum	Mo	313.259	I	30
Nickel	Ni	232.003	I	5
Osmium	Os	290.906	I	17,000
Palladium	Pd	244.791	I	2000
		247.642	I	30
Platinum	Pt	265.945	I	100
Potassium	K	766.490	I	5
Rhodium	Rh	343.489	I	30
Rubidium	Rb	420.180	I	NA
		780.027	I	5
Ruthenium	Ru	349.894	I	300
		372.803	I	3000
Selenium	Se	196.09	I	100
		203.98	I	2000
Silver	Ag	328.068	I	5
		338.289	I	200
Sodium	Na	330.237	I	NA
		588.9950	I	2
		589.5924	I	2
Strontium	Sr	407.771	II	NA
		460.733	I	10
Tellurium	Te	214.281	I	100
Thallium	Tl	276.787	I	30
		377.572	I	2400
Tin	Sn	224.605	I	30
Zinc	Zn	213.856	I	2

*Note:* These data were taken from Reference 2.

<sup>a</sup> Flames formed from air combined with the lighter hydrocarbons, such as methane, propane, butane, or natural gas, behave in a very similar fashion with similar temperatures, similar chemical properties, etc.

**Limits of Detection for the Air–Acetylene Flame**

<b>Element</b>	<b>Symbol</b>	<b>Wavelength (nm)</b>	<b>Type</b>	<b>LOD-AES (ppb)</b>	<b>LOS-AAS (ppb)</b>
Aluminum	Al	308.2153	I	NO	700
		309.2710	I	NO	500
		396.1520	I	NA	600
Antimony	Sb	206.833	I	NA	50
		217.581	I	NA	40
		231.147	I	3000	40
		259.805	I	NA	NO
Arsenic	As	193.759	I	10,000	140
Barium	Ba	455.403	II	NA	NO
		553.548	I	NA	NO
Bismuth	Bi	223.061	I	3000	25
Boron	B	249.677	I	NA	NO
Cadmium	Cd	228.8022	I	500	1
		326.1055	I	NA	NA
Calcium	Ca	393.366	II	NO	5000
		396.847	II	NO	5000
		422.673	I	0.5	0.5
Cesium	Cs	455.5276	I	NA	NO
		852.1122	I	NA	8
Chromium	Cr	357.869	I	NA	3
		425.435	I	NA	200
Cobalt	Co	240.725	I	NO	4
		352.685	I	NA	125
Copper	Cu	324.754	I	NA	1
		327.396	I	NA	120
Gallium	Ga	287.424	I	NO	50
		294.364	I	NA	50
		417.204	I	NA	1500
Germanium	Ge	265.1172	I	7000	
Gold	Au	242.795	I	NA	6
		267.595	I	NA	90
Indium	In	303.936	I	NA	30
		325.609	I	NA	20
		451.131	I	NA	200
Iodine	I	183.038	I	NO	8000
		206.163	I	2,500,000	NO
Iridium	Ir	208.882	I	NO	600
		2639.71	I	NO	2500
Iron	Fe	248.3271	I	NO	5
		371.9935	I	NA	700
Lead	Pb	217.000	I	NO	9
		283.3053	I	NA	240
		368.3462	I	NA	NO
Lithium	Li	670.776	I	NA	0.3
		451.857	I	NO	NA
Magnesium	Mg	279.553	II	NO	NA
		280.270	II	NO	NA
		285.213	I	NA	0.1
Manganese	Mn	279.482	I	NA	2
		403.076	I	NA	600
Mercury	Hg	253.652	I	NA	140
Molybdenum	Mo	313.259	I	NO	20
		379.825	I	80,000	900
		390.296	I	100	1600
Nickel	Ni	232.003	I	NO	2
		352.454	I	NA	350
Niobium	Nb	309.418	II	NO	NA
Osmium	Os	290.906	I	NA	1200

**Limits of Detection for the Air–Acetylene Flame (continued)**

<b>Element</b>	<b>Symbol</b>	<b>Wavelength (nm)</b>	<b>Type</b>	<b>LOD-AES (ppb)</b>	<b>LOS-AAS (ppb)</b>
Palladium	Pd	244.791	I	NO	20
		247.642	I	NO	20
		340.458	I	NA	660
		363.470	I	NA	300
Phosphorus	P	213.547	I	NO	30,000
Platinum	Pt	214.423	I	NO	350
		265.945	I	NA	50
Potassium	K	766.490	I	NA	1
Rhenium	Re	346.046	I	NO	800
Rhodium	Rh	343.489	I	NA	2
		369.236	I	NA	70
Rubidium	Rb	420.180	I	NA	NO
		780.027	I	NA	0.3
Ruthenium	Ru	349.894	I	NA	400
		372.803	I	NA	250
Selenium	Se	196.09	I	NA	50
		203.98	I	50,000	10,000
Silver	Ag	328.068	I	NA	1
		338.289	I	NA	70
Sodium	Na	330.237	I	NO	NA
		588.9950	I	NA	1
		589.5924	I	NA	0.2
Strontium	Sr	407.771	II	NA	400
		421.552	II	NO	NA
		460.733	I	NA	2
Sulfur	S	180.7311	I	NO	30,000
Tellurium	Te	214.281	I	500	30
		238.578	I	NO	NA
Thallium	Tl	276.787	I	NA	30
		377.572	I	NA	1200
		535.046	I	NA	12,000
Tin	Sn	224.605	I	NO	10
		235.484	I	2000	600
		283.999	I	NA	1000
		326.234	I	NA	NO
Tungsten	W	255.135	I	90,000	3000
		400.875	I		
Uranium	U	591.539	I	NA	NO
Vanadium	V	318.540	I	NA	NO
		437.924	I	300	NO
Ytterbium	Yb	398.799	I	NO	80
Zinc	Zn	213.856	I	7000	1
Zirconium	Zr	351.960	I	NO	NA

*Note:* These data were taken from References 2 and 6.

# Limits of Detection for the Nitrous Oxide–Acetylene Flame

Element	Symbol	Wavelength (nm)	Type	LOD-AES (ppb)	LOD-AAS (ppb)
Aluminum	Al	308.2153	I	NA	NO
		309.2710	I	NA	20
		396.1520	I	3	900
Barium	Ba	553.548	I	1	8
Beryllium	Be	234.861	I	100	1
Boron	B	208.891	I	NO	NA
		208.957	I	NO	24,000
		249.677	I	NO	700
		249.773	I	NO	1500
Cadmium	Cd	326.1055	I	800	NO
Calcium	Ca	422.673	I	0.1	1
Cesium	Cs	455.5276	I	600	NO
		852.1122	I	0.02	NO
Chromium	Cr	425.435	I	1	NO
Cobalt	Co	352.685	I	200	NO
Copper	Cu	324.754	I	30	NO
		327.396	I	3	NO
Dysprosium	Dy	353.170	II	NO	800
		404.597	I	20	500
		421.172	I	NO	50
Erbium	Er	337.271	II	NO	100
		400.796	I	20	40
Europium	Eu	459.403	I	0.2	30
Gadolinium	Gd	368.413	I	NO	2000
		440.186	I	1000	NO
Gallium	Ga	417.204	I	5	NO
Germanium	Ge	265.1172	I	400	50
Gold	Au	267.595	I	500	NO
Hafnium	Hf	307.288	I	NO	2000
Holmium	Ho	345.600	II	NO	3000
		405.393	I	10	400
		410.384	I	NO	40
Indium	In	303.936	I	NO	1000
		325.609	I	NO	700
		451.131	I	1	3500
Iridium	Ir	208.882	I	NO	500
Iron	Fe	371.9935	I	10	NO
Lanthanum	La	408.672	II	NO	7500
		550.134	I	4000	2000
Lead	Pb	368.3462	I	0.2	NO
Lithium	Li	670.776	I	0.001	NO
Lutetium	Lu	261.542	II	NO	3000
		451.857	I	400	NO
Magnesium	Mg	285.213	I	1	NO
Manganese	Mn	403.076	I	1	NO
Mercury	Hg	253.652	I	10,000	NO
Molybdenum	Mo	313.259	I	10	25
		379.825	I	300	NO
		390.296	I	10	NO
Neodymium	Nd	463.424	I	200	600
		492.453	I		700
Nickel	Ni	352.454	I	20	NO
Niobium	Nb	334.906	I	NO	1000
		405.894	I	60	5000
Osmium	Os	290.906	I	NO	80
		442.047	I	2000	NA
Palladium	Pd	363.470	I	40	NO
Phosphorus	P	177.499	I	NO	30,000
		213.547	I	NO	29,000
Platinum	Pt	265.945	I	2000	2000

Limits of Detection for the Nitrous Oxide–Acetylene Flame (continued)

Element	Symbol	Wavelength (nm)	Type	LOD-AES (ppb)	LOD-AAS (ppb)
Potassium	K	766.490	I	0.01	NO
Praseodymium	Pr	495.137	I	500	2000
Rhenium	Re	364.046	I	200	200
Rhodium	Rh	343.489	I	NO	700
		369.236	I	10	1400
Rubidium	Rb	780.027	I	8	NO
Ruthenium	Ru	372.803	I	300	NO
Samarium	Sm	429.674	I	NO	500
		476.027	I	50	14,000
Scandium	Sc	391.181	I	10	20
Selenium	Se	196.09	I	100,000	NO
Silicon	Si	251.6113	I	3000	20
		288.1579	I	NO	NA
Silver	Ag	328.068	I	2	NO
Sodium	Na	588.9950	I	0.01	NO
		589.5924	I	0.01	NO
Strontium	Sr	469.733	I	0.1	50
Tantalum	Ta	271.467	I	NO	800
		474.016	I	4000	NO
Terbium	Tb	432.643	I	NA	600
Thallium	Tl	377.572	I	50	NO
		535.046	I	2	
Thorium	Th	324.4448	I	NO	181,000
		491.9816	II	10,000	NO
Thulium	Tm	371.791	I	4	10
Tin	Sn	224.605	I	NO	3000
		235.484	I	NO	90
		283.999	I	100	NO
Titanium	Ti	334.941	II	NO	NA
		364.268	I	NA	10
		365.350	I	30	500
Tungsten	W	255.135	I	NO	500
		400.875	I	200	7500
Uranium	U	358.488	I	NO	7000
Vanadium	V	318.540	I	200	20
		437.924	I	7	100
Ytterbium	Yb	398.799	I	0.2	5
Yttrium	Y	410.238	I	NO	50
Zinc	Zn	213.856	I	10,000	NO
Zirconium	Zr	351.960	I	1200	NO
		360.119	I	3000	1000

*Note:* These data were taken from References 2 and 6.

Limits of Detection for Graphite Furnace AAS<sup>a</sup>

Element	Symbol	Wavelength (nm)	Type	LOD (ppb)
Aluminum	Al	308.2153	I	NA
		309.2710	I	0.01
		396.1520	I	600
Antimony	Sb	206.833	I	NA
		217.581	I	0.08
		231.147	I	NA
Arsenic	As	189.042	I	NA
		193.759	I	0.12
Barium	Ba	553.548	I	0.04
Beryllium	Be	234.861	I	0.003
Bismuth	Bi	223.061	I	0.01
Cadmium	Cd	228.8022	I	0.0002
Calcium	Ca	422.673	I	0.01
Chromium	Cr	357.869	I	0.004
Cobalt	Co	240.725	I	8
Copper	Cu	324.754	I	0.005
		327.396	I	NA
Erbium	Er	400.796	I	0.3
Gadolinium	Gd	440.186	I	0.3
Gallium	Ga	287.424	I	0.01
Germanium	Ge	265.1172	I	0.1
Gold	Au	242.795	I	0.01
Holmium	Ho	345.600	II	NA
		405.393	I	NA
Indium	In	303.936	I	0.02
Iodine	I	183.038	I	40,000
Iridium	Ir	208.882	I	0.5
Iron	Fe	248.3271	I	0.01
		371.9935	I	NA
Lanthanum	La	550.134	I	0.5
Lead	Pb	217.000	I	0.007
		283.3053	I	NA
Lithium	Li	670.776	I	0.01
Magnesium	Mg	285.213	I	0.0002
Manganese	Mn	279.482	I	0.0005
		403.076	I	NA
Mercury	Hg	253.652	I	0.2
Molybdenum	Mo	313.259	I	0.03
Nickel	Ni	232.003	I	0.05
Osmium	Os	290.906	I	2
Palladium	Pd	247.642	I	0.05
Phosphorus	P	177.499	I	NA
		213.547	I	20
		253.561	I	NA
Platinum	Pt	265.945	I	0.2
Potassium	K	766.490	I	0.004
Rhenium	Re	346.046	I	10
Rhodium	Rh	343.489	I	0.1
Rubidium	Rb	780.027	I	NA
Selenium	Se	196.09	I	0.05
Silicon	Si	251.6113	I	0.6
Silver	Ag	328.068	I	0.001
Sodium	Na	588.9950	I	0.004
Strontium	Sr	460.733	I	0.01
Sulfur	S	180.7311	I	NA
		182.0343	I	NA
		216.89	I	NA
Tellurium	Te	214.281	I	0.03
Thallium	Tl	276.787	I	0.01

Limits of Detection for Graphite Furnace AAS<sup>a</sup> (continued)

Element	Symbol	Wavelength (nm)	Type	LOD (ppb)
Tin	Sn	235.484	I	0.03
		283.999	I	NA
Titanium	Ti	364.268	I	0.3
		365.350	I	NA
Uranium	U	358.488	I	30
Vanadium	V	318.540	I	0.4
Ytterbium	Yb	398.799	I	0.01
Yttrium	Y	410.238	I	10
Zinc	Zn	213.856	I	0.001

<sup>a</sup> The detection limits for the graphite furnace AAS are calculated using 100  $\mu$ l of sample. In graphite furnace AAS, additional chemicals are often added to aid in determining certain elements. Walter Slavin has published an excellent guide to these issues and has provided an excellent bibliography: Slavin, W., *Graphite Furnace Source Book*, Perkin-Elmer Corp., Ridgefield, CT, 1984; and Slavin, W. and Manning, D.C., Furnace interferences, a guide to the literature, *Prog. Anal. Spectrosc.*, 5, 243, 1982.

Limits of Detection for ICP-AES

Element	Symbol	Wavelength (nm)	Type	LOD (ppb)	Reference
Aluminum	Al	167.0787	II	1	6
		308.2153	I	0.4	7
		309.2710	I	0.02	8
		396.1520	I	0.2	7
Antimony	Sb	206.833	I	10	7
		217.581	I	15	7
		231.147	I	61	7
		259.805	I	107	7
Arsenic	As	189.042	I	136	8
		193.759	I	2	7
		197.262	I	76	7
		234.984	I	90	7
Barium	Ba	455.403	II	0.001	8
		493.409	II	0.3	7
		553.548	I	2	7
Beryllium	Be	234.861	I	0.003	7
		313.042	II	0.1	6
		313.107	II	0.01	8
Bismuth	Bi	223.061	I	0.03	8
		289.798	I	10	7
Boron	B	208.891	I	5	8
		208.957	I	3	8
		249.677	I	0.1	8
		249.773	I	2	8
Bromine	Br	470.486	II	NA	8
		827.244	I	NA	8
Cadmium	Cd	214.441	II	0.1	8
		226.502	II	0.05	8
		228.8022	I	0.08	8
		326.1055	I	3	8
Calcium	Ca	364.441	I	0.5	8
		393.366	II	0.0001	8
		396.847	II	0.002	8
		422.673	I	0.2	8
Carbon	C	193.0905	I	40	6
		247.856	I	100	8
Cerium	Ce	394.275	II	2	8
		413.765	II	40	6
		418.660	II	0.4	7



Limits of Detection for ICP-AES (continued)

Element	Symbol	Wavelength (nm)	Type	LOD (ppb)	Reference
Chlorine	Cl	413.250	II	NA	7
		837.594	I	NA	8
Chromium	Cr	205.552	II	0.009	8
		267.716	II	0.08	8
		357.869	I	0.1	8
		425.435	I	5	8
Cobalt	Co	228.615	II	0.3	8
		238.892	II	0.1	7
Copper	Cu	213.5981	II	7	8
		324.754	I	0.01	8
		327.396	I	0.06	8
Dysprosium	Dy	353.170	II	1	8
Erbium	Er	337.271	II	1	8
		400.796	I	1	7
Europium	Eu	381.967	II	0.06	7
Fluorine	F	685.603	I	NA	8
Gadolinium	Gd	342.247	II	0.4	7
Gallium	Ga	287.424	I	78	7
		294.364	I	3	8
		417.204	I	0.6	8
Germanium	Ge	199.8887	I	0.6	8
		209.4258	I	11	8
		265.1172	I	4	7
Gold	Au	242.795	I	2	8
		267.595	I	0.9	7
Hafnium	Hf	277.336	II	2	8
		339.980	II	5	6
Holmium	Ho	345.600	II	1	6
		389.102	II	0.9	8
Hydrogen	H	486.133	I	NA	8
		656.2852	I	NA	7
Indium	In	230.605	II	30	8
		303.936	I	15	8
		325.609	I	15	6
		451.131	I	30	7
Iodine	I	183.038	I	NA	7
		206.163	I	10	8
Iridium	Ir	224.268	II	0.6	8
		2639.71	I	0.6	8
Iron	Fe	238.204	II	0.004	8
		259.9396	II	0.09	7
		371.9935	I	0.3	7
Lanthanum	La	333.749	II	2	6
		408.672	II	0.1	8
Lead	Pb	217.000	I	30	8
		220.3534	II	0.6	8
		283.3053	I	2	7
		368.2462	I	20	8
Lithium	Li	670.776	I	0.02	7
Lutetium	Lu	261.542	II	0.1	7
		451.857	I	8	7
Magnesium	Mg	279.553	II	0.003	7
		280.270	II	0.01	7
		285.231	I	0.2	7
Manganese	Mn	257.610	II	0.01	7
		403.076	I	0.6	7
Mercury	Hg	184.905	II	1	7
		194.227	II	10	6
		253.652	I	1	7

Limits of Detection for ICP-AES (continued)

Element	Symbol	Wavelength (nm)	Type	LOD (ppb)	Reference
Molybdenum	Mo	202.030	II	0.3	8
		313.259	I	NA	8
		379.825	I	0.2	7
		390.296	I	80	8
Neodymium	Nd	401.225	II	0.3	7
Nickel	Ni	221.648	II	2	8
		232.003	I	6	8
		352.454	I	0.2	7
Niobium	Nb	309.418	II	0.2	7
Nitrogen	N	174.2729	I	1000	8
		821.634	I	27,000	8
Osmium	Os	225.585	II	4	8
		290.906	I	6	8
Oxygen	O	426.825	I	NA	8
		777.194	I	NA	8
Palladium	Pd	340.458	I	2	8
		363.470	I	1	8
Phosphorus	P	177.499	I	NA	8
		213.547	I	16	6
		253.561	I	15	7
Platinum	Pt	214.423	I	16	6
		265.945	I	0.9	7
Potassium	K	766.490	I	5	8
Praseodymium	Pr	390.805	II	0.3	8
		422.535	II	10	7
Rhenium	Re	197.3	?	6	7
		221.426	II	4	6
Rhodium	Rh	233.477	II	30	7
		343.489	I	8	6
		369.236	I	7	8
Rubidium	Rb	420.180	I	38,000	8
		780.027	I	100	6
Ruthenium	Ru	240.272	II	8	6
		349.894	I	NA	8
		372.803	I	60	7
Samarium	Sm	359.260	II	0.5	8
		373.912	II	2	7
Scandium	Sc	361.384	II	0.1	8
Selenium	Se	196.09	I	0.1	8
		203.98	I	0.03	8
Silicon	Si	251.6113	I	2	7
		288.1579	I	10	7
Silver	Ag	328.068	I	0.8	8
		338.289	I	7	8
Sodium	Na	330.237	I	100	8
		588.9950	I	0.1	7
		589.5924	I	0.5	8
Strontium	Sr	407.771	II	0.2	6
		421.552	II	0.1	8
		460.733	I	0.4	8
Sulfur	S	180.7311	I	15	6
		182.0343	I	30	7
		216.89		NA	7
Tantalum	Ta	226.230	II	15	8
		240.063	II	13	6
		296.513	II	5	7
Tellurium	Te	214.281	I	0.7	8
		238.578	I	2	8
Terbium	Tb	350.917	II	0.1	7
		367.635	II	1.5	8

Limits of Detection for ICP-AES (continued)

Element	Symbol	Wavelength (nm)	Type	LOD (ppb)	Reference
Thallium	Tl	190.864	II	4	8
		276.787	I	27	6
		377.572	I	17	8
Thorium	Th	283.7295	II	8	6
		401.9129	II	1.3	8
Thulium	Tm	313.126	II	0.9	6
		346.220	II	0.2	7
Tin	Sn	189.991	II	0.05	8
		235.484	I	9	8
		283.999	I	10	8
		326.234	I	0.5	8
Titanium	Ti	334.941	II	0.1	8
		365.350	I	230	8
		368.520	II	0.2	8
Tungsten	W	207.911	II	7	8
		276.427	II	0.8	7
		400.875	I	3	7
Uranium	U	263.553	II	70	6
		385.957	II	2	7
Vanadium	V	309.311	II	0.06	7
		311.062	II	0.06	7
		437.924	I	0.2	7
Ytterbium	Yb	328.937	II	0.01	8
		369.419	II	0.02	7
Yttrium	Y	371.030	II	0.04	7
		377.433	II	0.1	8
Zinc	Zn	202.548	II	0.6	8
		213.856	I	0.07	8
Zirconium	Zr	343.823	II	0.06	7

## DETECTION LIMITS BY HYDRIDE GENERATION AND COLD VAPOR AAS

In addition to the AAS methods in flames or graphite furnaces, the elements listed below are detected and determined at extreme sensitivity by introduction into a flame or a hot quartz cell by AAS.

**Detection Limits by Hydride Generation and Cold Vapor AAS**

Element	Wavelength <sup>a</sup> (nm)	LOD <sup>b</sup> (ppb)
Antimony, Sb	217.581	0.1
Arsenic, As	193.759	0.02
Bismuth, Bi	223.061	0.02
Mercury, Hg	313.652	0.02
Selenium, Se	196.09	0.02
Tellurium, Te	214.281	0.02
Tin, Sn	235.484	0.5

*Note:* These data were taken from Reference 9.

<sup>a</sup> It has been assumed that the transitions used for these detection limits were the most sensitive cited for AAS.

<sup>b</sup> The detection limits are based on 50-ml sample solution volumes.

## SPECTRAL OVERLAPS

In FAES and FAAS, the analytical results will be totally degraded if there is a spectral overlap of an analyte transition. This can result from an interfering matrix element with a transition close to that of the analyte. This table presents a list of those overlaps that have been observed and those that are predicted to happen. In many cases the interferant element has been present in great excess when compared to the analyte species. Therefore, if the predicted interferant element is a major component of the matrix, a careful investigation for spectral overlap should be made. Excitation sources other than flames were not covered in this study.

Spectral Overlaps			
Analyte Element	Wavelength (nm)	Interfering Element	Wavelength (nm)
<b>Observed Overlaps</b>			
Aluminum	308.2153	Vanadium	308.211
Antimony	217.023	Lead	217.000
Antimony	231.147	Nickel	231.096
Cadmium	228.8022	Arsenic	228.812
Calcium	422.673	Germanium	422.6562
Cobalt	252.136	Indium	252.137
Copper	324.754	Europium	324.755
Gallium	403.299	Manganese	403.307
Iron	271.9027	Platinum	271.904
Manganese	403.307	Gallium	403.299
Mercury	253.652	Cobalt	253.649
Silicon	250.690	Vanadium	250.690
Zinc	213.856	Iron	213.859
<b>Predicted Overlaps</b>			
Boron	249.773	Germanium	249.7962
Bismuth	202.121	Gold	202.138
Cobalt	227.449	Rhenium	227.462
Cobalt	242.493	Osmium	242.497
Cobalt	252.136	Tungsten	252.132
Cobalt	346.580	Iron	346.5860
Cobalt	350.228	Rhodium	350.252
Cobalt	351.348	Iridium	351.364
Copper	216.509	Platinum	216.517
Gallium	294.417	Tungsten	294.440
Gold	242.795	Strontium	242.810
Hafnium	295.068	Niobium	295.088
Hafnium	302.053	Iron	302.0639
Indium	303.936	Germanium	303.9067
Iridium	208.882	Boron	208.891
Iridium	248.118	Tungsten	248.144
Iron	248.3271	Tin	248.339
Lanthanum	370.454	Vanadium	370.470
Lead	261.3655	Tungsten	261.382
Molybdenum	379.825	Niobium	379.812
Osmium	247.684	Nickel	247.687
Osmium	264.411	Titanium	264.426
Osmium	271.464	Tantalum	271.467
Osmium	285.076	Tantalum	285.098

**Spectral Overlaps (continued)**

<b>Analyte Element</b>	<b>Wavelength (nm)</b>	<b>Interfering Element</b>	<b>Wavelength (nm)</b>
Osmium	301.804	Hafnium	301.831
Palladium	363.470	Ruthenium	363.493
Platinum	227.438	Cobalt	227.449
Rhodium	350.252	Cobalt	350.262
Scandium	298.075	Hafnium	298.081
Scandium	298.895	Ruthenium	298.895
Scandium	393.338	Calcium	393.366
Silicon	252.4108	Iron	252.4293
Silver	328.068	Rhodium	328.055
Strontium	421.552	Rubidium	421.553
Tantalum	263.690	Osmium	263.713
Tantalum	266.189	Iridium	266.198
Tantalum	269.131	Germanium	269.1341
Thallium	291.832	Hafnium	291.858
Thallium	377.572	Nickel	377.557
Tin	226.891	Aluminum	226.910
Tin	266.124	Tantalum	266.134
Tin	270.651	Scandium	270.677
Titanium	264.664	Platinum	264.689
Tungsten	265.654	Tantalum	265.661
Tungsten	271.891	Iron	271.9027
Vanadium	252.622	Tantalum	252.635
Zirconium	301.175	Nickel	301.200
Zirconium	386.387	Molybdenum	386.411
Zirconium	396.826	Calcium	396.847

*Note:* These data were taken from Reference 10.

## RELATIVE INTENSITIES OF ELEMENTAL TRANSITIONS FROM HOLLOW CATHODE LAMPS

In AAS the hollow cathode lamp (HCL) is the most important excitation source for most of the elements determined. However, sufficient light must reach the detector for the measurement to be made with good precision and detection limits. For elements in this table with intensities of less than 100, HCLs are probably inadequate, and other sources such as electrodeless discharge lamps should be investigated.

Relative Intensities of Elemental Transitions from Hollow Cathode Lamps			
Element	Fill Gas	Wavelength (nm)	Relative Emission Intensity <sup>a</sup>
Aluminum	Ne	309.2710	1200
		309.2839	800
		396.1520	
Antimony	Ne	217.581	250
		231.147	250
Arsenic	Ar	193.759	125
		197.262	125
Barium	Ne	553.548	400
		350.111	200
Beryllium	Ne	234.861	2500
Bismuth	Ne	223.061	120
		306.772	400
Boron	Ar	249.773	400
Cadmium	Ne	228.8022	2500
		326.1055	5000
Calcium	Ne	422.673	1400
Cerium	Ne	520.012	8
		520.042	8
		569.699	
Chromium	Ne	357.869	6000
		425.435	5000
Cobalt	Ne	240.725	1000
		345.350	1500
		352.685	1300
Copper	Ne	324.754	7000
		327.396	6000
Dysprosium	Ne	404.597	2000
		418.682	2000
		421.172	2500
Erbium	Ne	400.796	1600
		386.285	1600
Europium	Ne	459.403	1000
		462.722	950
Gadolinium	Ne	368.413	350
		407.870	700
Gallium	Ne	287.424	400
		417.204	1100
Germanium	Ne	265.1172	500
		265.1568	250
		259.2534	
Gold	Ne	242.795	750
		267.595	1200
Hafnium	Ne	307.288	300
		286.637	200

**Relative Intensities of Elemental Transitions from Hollow Cathode Lamps (continued)**

<b>Element</b>	<b>Fill Gas</b>	<b>Wavelength (nm)</b>	<b>Relative Emission Intensity<sup>a</sup></b>
Holmium	Ne	405.393	2000
		410.384	2200
Indium	Ne	303.936	500
		410.176	500
Iridium	Ne	263.971	400
Iron	Ne	248.3271	400
		371.9935	2400
Lanthanum	Ne	550.134	120
		392.756	45
Lead	Ne	217.000	200
		283.3053	1000
Lithium	Ne	670.776	700
Lutetium	Ar	335.956	30
		337.650	25
		356.784	15
Magnesium	Ne	285.213	6000
		202.582	130
Manganese	Ne	279.482	3000
		280.106	2200
		403.076	14,000
Mercury	Ar	253.652	1000
Molybdenum	Ne	313.259	1500
		317.035	800
Neodymium	Ne	463.424	300
		492.453	600
Nickel	Ne	232.003	1000
		341.476	2000
Niobium	Ne	405.894	400
		407.973	360
Osmium	Ar	290.906	400
		301.804	200
Palladium	Ne	244.791	400
		247.642	300
		340.458	3000
Phosphorus	Ne	215.547	30
		213.618	20
		214.914	
Platinum	Ne	265.945	1500
		299.797	1000
Potassium	Ne	766.490	6
		404.414	300
Praseodymium	Ne	495.137	100
		512.342	70
Rhenium	Ne	346.046	1200
		346.473	900
Rhodium	Ne	343.489	2500
		369.236	2000
		350.732	200
Rubidium	Ne	780.027	1.5
		420.180	80
Ruthenium	Ar	349.894	600
		392.592	300
Samarium	Ne	429.674	600
		476.027	800



**Relative Intensities of Elemental Transitions from Hollow Cathode Lamps (continued)**

<b>Element</b>	<b>Fill Gas</b>	<b>Wavelength (nm)</b>	<b>Relative Emission Intensity<sup>a</sup></b>
Scandium	Ne	391.181	3000
		390.749	2500
		402.040	1800
		402.369	2100
Selenium	Ne	196.09	50
		203.98	50
Silicon	Ne	251.6113	500
		288.1579	500
Silver	Ar	328.068	3000
		338.289	3000
Sodium	Ne	588.9950	2000
		330.237	40
		330.298	
Strontium	Ne	460.733	1000
Tantalum	Ar	271.467	150
		277.588	100
Tellurium	Ne	214.281	60
		238.578	50
Terbium	Ne	432.643	110
		432.690	90
		431.883	60
		433.841	
Thallium	Ne	276.787	600
		258.014	50
Thulium	Ne	371.791	40
		409.419	50
		410.584	70
Tin	Ne	224.605	100
		286.332	250
Titanium	Ne	364.268	600
		399.864	600
Tungsten	Ne	255.100	200
		255.135	1400
		400.875	
Uranium	Ne	358.488	300
		356.659	200
		351.461	200
		348.937	150
Vanadium	Ne	318.314	600
		318.398	200
		385.537	
		385.584	
Ytterbium	Ar	398.799	2000
		346.437	800
Yttrium	Ne	407.738	500
		410.238	600
		414.285	300
Zinc	Ne	213.856	2500
		307.590	2500

*Note:* These data were obtained using Westinghouse HCLs and a single experimental setup. No correction has been made for the spectral response of the monochromator/photomultiplier tube system. These data were taken from Reference 2.

<sup>a</sup> The most intense line is the Mn 403.076 transition with a relative intensity of 14,000.

## INERT GASES

In AAS, the excitation source inert gas emission offers a potential background spectral interference. The most common inert gases used in hollow cathode lamps are Ne and Ar. The data taken for this table and the other tables in this book on lamp spectra are from HCLs; however, electrodeless discharge lamps emit very similar spectra. The emission spectra for Ne and Ar HCLs and close lines that must be resolved for accurate analytical results are provided in the following four tables. This information was obtained for HCLs and flame atom cells and should not be considered with respect to plasma sources. In the “Type” column, I indicates that the transition originates from an atomic species and II indicates a singly ionized species.

### Neon Hollow Cathode Lamp Spectrum

Wavelength (nm)	Type	Relative Intensity <sup>a</sup>
323.237	II	5.4
330.974	II	2.8
331.972	II	8.7
332.374	II	28
332.916	II	1.7
333.484	II	5.2
334.440	II	17
335.502	II	3.5
336.060	II	1.7
336.9908	I	7.8
336.9908	II	17
337.822		
339.280	II	8.3
341.7904	I	16
344.7703	I	12
345.4195	I	15
346.0524	I	6.6
346.6579	I	12
347.2571	I	12
349.8064	I	2.9
350.1216	I	3.8
351.5191	I	3.6
352.0472	I	61
356.850	II	7.8
357.461	II	5.9
359.3526	I	19
360.0169	I	3.5
363.3665	I	3.6
366.407	II	1.9
369.421	II	3.5
370.962	II	4.9
372.186	II	3.1
404.264	I	1.4
533.0778	I	1.6
534.920	I	1.6
540.0562	I	3.3
576.4419	I	2.3
585.2488	I	100
588.1895	I	8.7
594.4834	I	14
597.4627	I	2.6
597.5534	I	
602.9997	I	2.8
607.4338	I	11
609.6163	I	15
614.3063	I	20
616.3594	I	5.2

*Note:* These data were taken with a Varian copper HCL operated at 10 mA. The Cu 324.7-nm transition was a factor of 2.9 more intense than the 585.249-nm Ne transition. The spectrum was taken with an IP28 photomultiplier tube (PMT). The relative intensities were not corrected for the instrumental/PMT response. These data were taken from Reference 2.

<sup>a</sup> These data are referenced to the Ne transition at 585.2488 nm, which has been assigned the value of 100.

### Neon Lines That Must Be Resolved for Accurate AAS Measurements

Analyte Element	Wavelength (nm)	Neon Line (nm)	Required Resolution (nm) <sup>a</sup>
Chromium	357.869	357.461	0.20
Chromium	359.349	359.3526	0.002
Chromium	360.533	360.0169	0.26
Copper	324.754	323.237	0.75
Dysprosium	404.597	404.264	0.17
Gadolinium	371.357	370.962	0.20
Gadolinium	371.748	372.186	0.22
Lithium	670.776	335.502 in 2nd order is 671.004	0.11
Lutetium	335.956	336.060	0.05
Niobium	405.894	404.264	0.82
Rhenium	346.046	346.0524	0.003
Rhenium	346.473	346.6579	0.11
Rhenium	345.188	345.4195	0.12
Rhodium	343.489	344.7703	0.64
Rhodium	369.236	369.421	0.09
Ruthenium	372.803	372.186	0.31
Scandium	402.369	404.264	0.94
Silver	338.289	337.822	0.23
Sodium	588.995	588.1895	0.40
Sodium	589.592	588.1895	0.70
Thulium	371.792	372.186	0.19
Titanium	337.145	336.9808 and 336.9908	0.08
Titanium	364.268	363.3665	0.45
Titanium	365.350	366.407	0.53
Uranium	356.660	356.850	0.09
Uranium	358.488	359.3526	0.43
Ytterbium	346.436	346.6579	0.11
Zirconium	351.960	352.0472	0.04
Zirconium	360.119	360.0169	0.05

*Note:* These data were taken from Reference 10.

<sup>a</sup> The monochromator settings must be at least one half of the separation of the analyte and interferant transition.

### Argon Hollow Cathode Lamp Spectrum

Wavelength (nm)	Type	Relative Intensity <sup>a</sup>
294.2893	II	3.5
297.9050	II	1.9
329.3640	II	1.5
330.7228	II	1.5
335.0924	II	2.2
337.6436	II	2.2
338.8531	II	1.8
347.6747	II	3.7
349.1244	II	2.0
349.1536	II	7.2
350.9778	II	7.0
351.4388	II	4.0
354.5596	II	11
354.5845	II	12
355.9508	II	16
356.1030	II	1.8
357.6616	II	11
358.1608	II	3.9
358.2355	II	8.5
358.8441	II	1.2
360.6522	I	2.0
362.2138	II	1.3
363.9833	II	3.3
371.8206	II	5.5
372.9309	II	1.3
373.7889	II	9.8
376.5270	II	5.1
376.6119	II	6.8
377.0520	II	1.7
378.0840	II	4.0
380.3172	II	5.5
380.9456	II	1.8
383.4679	I	2.6
385.0581	II	1.2
386.8528	II	7.0
392.5719	II	9.9
392.8623	II	6.9
393.2547	II	3.2
394.6097	II	14
394.8979	I	5.2
397.9356	II	5.6
399.4792	II	6.2
401.3857	II	4.3
403.3809	II	2.5
403.5460	II	2.3
404.2894	II	1.6
404.4418	I	9.0
405.2921	II	21
407.2005	II	34
407.2385	II	5.5
407.6628	II	2.0
407.9574	II	4.4
408.2387	II	3.2
410.3912	II	10
413.1724	II	61
415.6086	II	2.4
415.8590	I	1.4

**Argon Hollow Cathode Lamp Spectrum (continued)**

<b>Wavelength (nm)</b>	<b>Type</b>	<b>Relative Intensity<sup>a</sup></b>
416.4180	I	4.4
418.1884	I	6.9
419.0713	I	9.1
419.1029	I	8.9
419.8317	I	38
420.0674	I	38
421.8665	II	2.2
422.2637	II	4.3
422.6988	II	5.6
422.8158	II	12
423.7220	II	15
425.1185	I	2.3
425.9326	I	42
426.6286	I	11
426.6527	II	7.4
427.2169	I	18
427.7528	II	100
428.2898	II	2.5
430.0101	I	13
430.0650	II	3.3
430.9239	II	6.6
433.1200	II	17
433.2030	II	4.2
433.3561	I	12
433.5338	I	5.8
434.5168	I	3.7
434.8064	II	1.5
435.2205	II	5.4
436.2066	II	3.3
436.7832	II	9.6
437.0753	II	32
437.1329	II	6.5
437.5954	II	10
437.9667	II	20
438.5057	II	6.7
440.0097	II	5.7
440.0986	II	15
442.6001	II	1.6
443.0189	II	1.2
443.0996	II	5.4
443.3838	II	5.3
443.9461	II	5.3
444.8879	II	7.9
447.4759	II	19
448.1811	II	33
451.0733	I	20
452.2323	I	2.0
453.0552	II	3.2
454.5052	II	1.3
457.9350	II	1.4
458.9898	II	47
459.6097	I	1.8
460.9567	II	1.3
462.8441	I	1.4
463.7233	II	5.5
465.7901	II	1.9
470.2316	I	2.5

**Argon Hollow Cathode Lamp Spectrum (continued)**

<b>Wavelength (nm)</b>	<b>Type</b>	<b>Relative Intensity<sup>a</sup></b>
472.6868	II	43
473.2053	II	9.7
473.5906	II	1.3
476.4865	II	1.5
480.6020	II	36
484.7812	II	1.6
486.5910	II	1.3
487.9864	II	58
488.9042	II	11
490.4752	II	3.5
493.3209	II	4.1
496.5080	II	28
500.9334	II	5.5
501.7163	II	12
506.2037	II	5.9
509.0495	II	2.9
514.1783	II	5.7
514.5308	II	3.7
516.2285	I	3.8
516.5773	II	1.8
518.7746	I	3.8
522.1271	I	1.2
545.1652	I	1.7
549.5874	I	3.1
555.8702	I	4.0
557.2541	I	1.9
560.6733	I	4.9
565.0704	I	1.7
588.8584	I	1.9
591.2085	I	4.1
592.8813	I	1.4
603.2127	I	4.1
604.3223	I	1.6
611.4923	II	2.2
617.2278	II	1.1
696.5431	I	3.2
706.7218	I	1.7
738.3980	I	1.2
750.3869	I	2.7

*Note:* These data were taken from an Ar-filled Ga HCL at the Los Alamos Fourier Transform Spectrometer facility.<sup>11</sup>

<sup>a</sup> These data are referenced to the Ar transition at 427.7528 nm, which has been assigned the value of 100.

## CLOSE LINES FOR BACKGROUND CORRECTION

In AAS, it is possible to make background corrections in many cases by measuring a normally nonabsorbing transition near the analytical transition. This table presents a list of suitable transitions for such a background measurement. It is often desirable to check the background absorbance by more than one method even if there is a built-in background measurement by some other means such as the continuum or Zeeman methods. In the table below, the first two columns give the analyte element and wavelength of the analytical transition, and the last two columns give the transition useful for the background measurement and its source. If the source is Ne and the HCL is Ne filled, the same HCL can be used for the background measurement; if not, a different HCL must be placed in the spectrometer to make the measurement.

Close Lines for Background Correction					
Element	Analysis Line (nm)		Background Line (nm)		Source
Aluminum	309.2711	I	306.614	I	Al
Antimony	217.581	I	217.919	I	Sb
Arsenic	231.147	I	231.398	I	Ni
Barium	193.759	I	191.294	II	As
	553.548	I	540.0562	I	Ne
			553.305	I	Mo
			557.742	I	Y
Beryllium	234.861	I	235.484	I	Sn
Bismuth	223.061	I	226.502	II	Cd
Bromine	306.772	I	306.614	I	Al
Cadmium	148.845	I	149.4675	I	N
	228.8022	I	226.502	II	Cd
Calcium	422.673	I	421.9360	I	Fe
Cesium	852.1122	I	423.5936	I	Fe
Chromium	357.869	I	854.4696	I	Ne
			352.0472	I	Ne
			358.119	I	Fe
Cobalt	204.206	I	238.892	II	Co
Copper	324.754	I	242.170	I	Sn
Dysprosium	421.172	I	324.316	I	Cu
			421.645	II	Fe
			421.096	I	Ag
Erbium	400.796	I	394.442	I	Er
Europium	459.403	I	460.102	I	Cr
Gallium	287.424	I	283.999	I	Sn
Gold	242.795	I	283.690	I	Cd
			242.170	I	Sn
Indium	303.936	I	306.614	I	Al
Iodine	183.038	I	184.445	I	I
Iron	248.3271	I	249.215	I	Cu
Lanthanum	550.134	I	550.549	I	Mo
			548.334	I	Co
Lead	283.3053	I	280.1995	I	Pb
Lithium	217.000	I	283.6900	I	Cd
Magnesium	670.791	I	220.3534	II	Pb
	285.213	I	671.7043	I	Ne
			283.690	I	Cd
			283.999	I	Sn
Manganese	279.482	I	282.437	I	Cu
Mercury	253.652	I	280.1995	I	Pb
Molybdenum	313.259	I	249.215	I	Cu
Nickel	232.003	I	312.200	II	Mo
			232.138	I	Ni



**Close Lines for Background Correction (continued)**

<b>Element</b>	<b>Analysis Line (nm)</b>		<b>Background Line (nm)</b>		<b>Source</b>
Palladium	247.642	I	249.215	I	Cu
Phosphorus	213.618	I	213.856	I	Zn
Potassium	766.490	I	769.896	I	K
Rhodium	343.489	I	767.209	I	Ca
			350.732	I	Rh
			352.0472	I	Ne
Rubidium	780.027	I	778.048	I	Ba
Ruthenium	249.894	I	352.0472	I	Ne
Selenium	196.09	I	199.51	I	Se
Silicon	251.6113	I	249.215	I	Cu
Silver	328.068	I	332.374	II	Ne
			326.234	I	Sn
Sodium	588.9950	I	588.833	I	Mo
Strontium	460.733	I	460.500	I	Ni
Tellurium	214.281	I	213.856	I	Zn
Thallium	276.787	I	217.581	I	Sb
			280.1995	I	Pb
Tin	224.605	I	226.502	II	Cd
Titanium	286.332	I	283.999	I	Sn
Uranium	364.268	I	361.939	I	Ni
	365.350	I	361.939	I	Ni
	358.488	I	358.119	I	Fe
Vanadium	318.398	I	324.754	I	Cu
Zinc	318.540	I	324.754	I	Cu
	213.856	I	212.274	II	Zn

*Note:* These data were taken from Reference 12.

## BETA VALUES FOR THE AIR-ACETYLENE AND NITROUS OXIDE-ACETYLENE FLAMES

Beta values represent the fraction of free atoms present in the hot flame gases of the flame indicated. These values have been taken from various sources and were either experimentally measured or calculated from thermodynamic data using the assumption of local thermodynamic equilibrium in the flame. These values do not have very good agreement within each element; however, the values do provide an indication of the probable sensitivity of the particular flame.

**Beta Values for the Air-Acetylene and Nitrous Oxide-Acetylene  
Flames**

Element	Symbol	Beta A/AC Flame	Beta N/AC Flame
Aluminum	Al	<0.0001	0.13
		<0.00005	0.29
		0.0005	0.97 <sup>a</sup>
			0.5
Antimony	Sb	0.03	
Arsenic	As	0.0002	
Barium	Ba	0.0009	0.074
		0.002	0.074
		0.003	0.98
		0.0018	
Beryllium	Be	0.0004	0.095
		0.00006	0.98
			0.98
Bismuth	Bi	0.17	0.35
Boron	B	<0.0006	0.0035
		<0.000001	0.2
Cadmium	Cd	0.38	0.56
		0.50	0.60
		0.80	
Calcium	Ca	0.066	0.34
		0.14	0.52 <sup>a</sup>
		0.05 <sup>a</sup>	0.98
		0.018	
Cesium	Cs	0.02	0.0004
		0.0057	
Chromium	Cr	0.071	0.63
		0.13	1.02
		0.53	1.00
		0.042	
Cobalt	Co	0.023	0.11
		0.28	0.25
		0.41	
Copper	Cu	0.4	0.49
		0.82	0.66
		0.98	1.00 <sup>a</sup>
Gallium	Ga	0.16	0.73
		0.16	
Germanium	Ge	0.001	
Gold	Au	0.21	0.16
		0.40	0.27
		0.63	
Indium	In	0.10	0.37
		0.67	0.93
		0.67	
Iridium	Ir	0.1	

**Beta Values for the Air–Acetylene and Nitrous Oxide–Acetylene  
Flames (continued)**

Element	Symbol	Beta A/AC Flame	Beta N/AC Flame
Iron	Fe	0.38	0.83
		0.66	0.91
		0.84	1.00
		0.66	
Lead	Pb	0.44	0.84
		0.77	
Lithium	Li	0.21	0.34 <sup>a</sup>
		0.26 <sup>a</sup>	0.96 <sup>a</sup>
		0.20 <sup>a</sup>	0.041
		0.08	0.91 <sup>a</sup>
Magnesium	Mg	0.59	0.88
		1.05	0.99
		0.62	0.92
			0.99 <sup>a</sup>
Manganese	Mn	0.45	0.37
		0.93	0.77
		1.0	
Mercury	Hg	0.04	
Molybdenum	Mo	0.03	
Nickel	Ni	1	
Palladium	Pd	1	
Platinum	Pt	0.4	
Potassium	K	0.7 <sup>a</sup>	0.12 <sup>a</sup>
		0.25	0.0004
		0.45	0.17 <sup>a</sup>
		0.59 <sup>a</sup>	
Rhodium	Rh	1	
Rubidium	Rb	0.16	
Ruthenium	Ru	0.3	
Selenium	Se	0.0001	
Silicon	Si	<0.001	0.55
		<0.0000001	0.12
			0.36
Silver	Ag	0.66	0.57
		0.70	
Sodium	Na	0.63	0.32
		1.00	0.97 <sup>a</sup>
		1.00 <sup>a</sup>	0.012
		0.56	0.80
Strontium	Sr	0.068	0.26
		0.10	0.57
		0.13	0.99
		0.021	
Tantalum	Ta		0.045
Thallium	Tl	0.36	0.55
		0.52	
Tin	Sn	<0.0001	0.35
		0.043	0.82
		0.078	
		0.061	
Titanium	Ti	<0.001	0.11
			0.33
			0.49

**Beta Values for the Air–Acetylene and Nitrous Oxide–Acetylene  
Flames (continued)**

Element	Symbol	Beta A/AC Flame	Beta N/AC Flame
Tungsten	W	0.004	0.71
Vanadium	V	0.0004	0.32
		0.015	0.99
		0.000001	
Zinc	Zn	0.66	0.49
		0.45	

*Note:* These data were taken from References 2 and 13.

<sup>a</sup> Ionization has been suppressed for these measurements/calculations.

## LOWER-ENERGY-LEVEL POPULATIONS (IN PERCENT) AS A FUNCTION OF TEMPERATURE

It is possible to calculate the relative number of atoms in the ground energy level(s) using the following equation:

$$\% \text{ Atoms (i}^{\text{th}} \text{ level)} = n_i/n_t * 100 = g_i/Z * \exp(-E_i/kT)$$

where  $n_i$  is the number of atoms in the  $i^{\text{th}}$  level per unit volume of atom cell,  $n_t$  is the total number of atoms per unit volume of atom cell,  $g_i$  is the statistical weight for energy level  $i$ ,  $Z$  is the electronic partition function,  $E_i$  is the energy of the  $i^{\text{th}}$  level,  $k$  is the Boltzmann constant, and  $T$  is the absolute temperature. Of course, all of the data must be in consistent units.

In utilizing these data, it should be remembered that, other things being equal, the larger the percentage of atoms in the ground or lower level of a transition, the larger the absorption signal from that transition should be. For example, a transition with 100% of the atoms in the ground state should be 10 times more sensitive than one with 10%. Also, these data refer to the percent of atoms in the atomic state only; therefore, this information should be used in conjunction with the beta values table.

**Lower-Energy-Level Populations (in Percent) as a Function  
of Temperature**

Element	Energy Level (cm <sup>-1</sup> )	Percent Population at Temperature (°C)		
		2000	2500	3000
Aluminum	0.0	35.1	34.8	34.5
	112.040	64.9	65.2	65.5
Antimony	0.0	99.7	98.7	97.0
	8512.100	0.2	0.7	1.6
	9854.100	0.1	0.5	1.7
Arsenic	0.0	99.9	99.5	98.5
	10592.500	0.0	0.2	0.6
	10914.600	0.1	0.3	0.8
Barium	0.0	98.0	92.6	82.6
	9033.985	0.4	1.5	3.3
	9215.518	0.6	2.3	5.0
	9596.551	0.7	2.6	5.8
	11395.382	0.1	0.7	1.8
Beryllium	0.0	100.0	100.0	100.0
Bismuth	0.0	100.0	99.8	99.5
Boron	0.0	33.5	33.5	33.5
	16.0	66.5	66.5	66.5
Cadmium	0.0	100.0	100.0	100.0
Calcium	0.0	100.0	99.8	99.3
	0.0	99.9	99.5	98.3
	11178.240	0.0	0.2	0.5
Cesium	111732.350	0.0	0.2	0.7
	0.0	98.6	95.9	91.5
	7593.160	0.3	0.9	1.7
Chromium	7750.780	0.1	0.2	0.3
	7810.820	0.1	0.2	0.3
	7927.470	0.1	0.4	0.9
	8095.210	0.2	0.7	1.3
	8307.570	0.3	0.8	1.7

**Lower-Energy-Level Populations (in Percent) as a Function  
of Temperature (continued)**

Element	Energy Level (cm <sup>-1</sup> )	Percent Population at Temperature (°C)		
		2000	2500	3000
Cobalt	0.0	51.8	45.6	40.9
	816.000	23.1	22.8	22.1
	1406.840	11.3	12.2	12.5
	1809.330	5.6	6.4	6.9
	3482.820	4.2	6.1	7.7
	4142.660	2.1	3.4	4.5
	4690.180	1.1	1.8	2.6
	5075.830	0.5	1.0	1.4
	7442.410	0.2	0.5	0.9
Copper	0.0	99.9	99.4	98.3
	11202.565	0.1	0.5	1.9
Gallium	0.0	47.5	44.6	42.6
	826.240	52.5	55.4	57.4
Germanium	0.0	20.6	18.2	16.6
	557.100	41.4	39.7	38.7
	1409.900	37.4	40.5	42.4
	7125.260	0.6	1.5	2.7
Gold	0.0	99.5	98.5	96.4
	9161.300	0.4	1.5	3.5
Hafnium	0.0	73.9	64.0	55.9
	2356.680	19.0	23.1	25.3
	4567.640	5.0	8.3	11.3
	5521.780	0.3	0.5	0.8
	5638.620	1.3	2.5	3.7
	6572.550	0.4	0.9	1.4
Indium	0.0	71.0	64.1	59.1
	2212.560	29.0	35.9	40.9
Iridium	0.0	85.1	77.2	69.9
	2834.980	11.1	15.1	18.0
	4078.940	1.8	3.0	4.0
	5784.620	0.8	1.7	2.6
	6323.910	0.7	1.6	2.7
	7106.610	0.4	1.0	1.9
Iron	0.0	46.2	43.4	41.0
	415.933	26.7	26.6	26.1
	704.003	15.5	16.1	16.3
	888.123	8.1	8.7	8.9
	978.074	2.5	2.7	2.9
	6928.280	0.4	1.0	1.8
	7376.775	0.2	0.6	1.2
	7728.071	0.1	0.4	0.8
	7985.795	0.1	0.2	0.5
Lanthanum	0.0	42.5	34.2	28.3
	1053.200	29.9	28.0	25.6
	2668.200	6.2	7.4	7.9
	3010.010	7.3	9.1	10.0
	3494.580	6.9	9.2	10.6
	4121.610	5.5	8.0	9.8
	7011.900	0.4	0.9	1.5
	7231.360	0.1	0.3	0.4
	7490.460	0.2	0.5	0.8
Lead	7679.940	0.3	0.6	1.1
	0.0	98.7	95.7	90.8
	7819.350	1.1	3.2	6.4
Lithium	10650.470	0.2	1.1	2.8
	0.0	100.0	99.9	99.8
Magnesium	0.0	100.0	100.0	100.0

**Lower-Energy-Level Populations (in Percent) as a Function  
of Temperature (continued)**

Element	Energy Level (cm <sup>-1</sup> )	Percent Population at Temperature (°C)		
		2000	2500	3000
Manganese	0.0	100.0	100.0	99.8
Mercury	0.0	100.0	100.0	100.0
Molybdenum	0.0	99.9	99.4	98.1
Nickel	0.0	39.5	36.4	34.2
	204.786	26.6	25.2	24.1
	879.813	11.7	12.2	12.4
	1332.153	11.8	13.2	14.0
	1713.080	3.9	4.5	5.0
	2216.519	4.5	5.7	6.6
	3409.925	1.9	2.8	3.7
Niobium	0.0	7.5	6.5	5.7
	154.190	13.4	11.8	10.6
	391.990	17.0	15.4	14.2
	695.250	18.2	17.3	16.4
	1050.260	17.6	17.7	17.3
	1142.790	6.6	6.7	6.6
	1586.900	7.2	7.8	8.0
	2154.110	6.4	7.5	8.1
	2805.360	5.0	6.4	7.5
	4998.170	0.2	0.4	0.5
	5297.920	0.3	0.6	0.9
	5965.450	0.3	0.6	1.0
Osmium	0.0	86.5	78.3	70.4
	2740.490	6.7	9.0	10.5
	4159.320	3.4	5.6	7.5
	5143.920	2.6	5.0	7.3
	5766.140	0.5	0.9	1.5
	6092.790	0.1	0.3	0.4
	8742.830	0.2	0.5	1.1
Palladium	0.0	91.7	80.3	67.2
	6464.110	6.2	13.8	21.6
	7754.990	1.8	4.7	8.3
	10093.940	0.2	0.7	1.6
	11721.770	0.1	0.5	1.2
Platinum	0.0	47.0	43.8	41.5
	775.900	19.2	20.0	20.4
	823.700	33.4	35.1	36.0
	6140.000	0.1	0.2	0.3
	6567.5000	0.3	0.7	1.3
Potassium	0.0	100.0	99.8	99.4
Rhenium	0.0	99.9	99.5	98.3
Rhodium	0.0	69.0	60.0	53.6
	1529.970	18.1	19.9	20.6
	2598.030	6.3	8.1	9.3
	3309.860	3.8	5.4	6.6
	3472.680	2.2	3.3	4.1
	5657.970	0.5	0.9	1.4
	5690.970	0.9	1.8	2.8
Rubidium	0.0	100.0	99.8	99.3

**Lower-Energy-Level Populations (in Percent) as a Function  
of Temperature (continued)**

Element	Energy Level (cm <sup>-1</sup> )	Percent Population at Temperature (°C)		
		2000	2500	3000
Ruthenium	0.0	62.4	55.2	49.3
	1190.640	21.7	22.8	22.8
	2091.540	8.8	10.6	11.5
	2713.240	4.0	5.3	6.1
	3105.490	1.8	2.5	3.0
	6545.030	0.5	1.0	1.8
	7483.070	0.2	0.6	1.1
	8084.120	0.1	0.3	0.7
	9183.660	0.0	0.1	0.3
Scandium	0.0	42.9	42.2	41.5
	168.340	57.0	57.4	57.4
Selenium	0.0	85.0	80.5	76.8
	1989.490	12.2	15.4	17.8
	2534.350	2.7	3.7	4.6
	9576.080	0.1	0.3	0.8
Silicon	0.0	12.3	11.9	11.6
	77.150	34.8	34.2	33.5
	223.310	52.2	52.3	52.1
	6298.810	0.7	1.6	2.8
Silver	0.0	100.0	100.0	100.0
Sodium	0.0	100.0	100.0	99.9
Strontium	0.0	100.0	99.8	98.9
Tantalum	0.0	64.9	53.8	45.0
	2010.00	23.0	25.4	25.8
	3963.920	7.5	11.0	13.5
	5621.040	2.9	5.3	7.6
	6049.420	0.4	0.8	1.2
	9253.430	0.1	0.4	0.8
	9705.380	0.1	0.4	0.9
Technetium	0.0	27.2	25.7	24.0
	170.132	33.8	32.6	31.0
	386.873	37.1	37.0	35.9
	6556.860	0.1	0.4	0.6
	6598.830	0.2	0.6	1.0
	6661.000	0.3	0.8	1.4
	6742.790	0.4	1.0	1.7
	6843.000	0.4	1.1	2.0
	7255.290	0.1	0.4	0.7
Tungsten	0.0	28.4	20.5	15.9
	1670.300	25.6	23.6	21.5
	2951.290	23.8	26.3	27.1
	3325.530	13.0	15.2	16.2
	4830.000	6.2	8.9	11.0
	6219.330	2.9	5.2	7.3
Vanadium	0.0	14.1	12.6	11.5
	137.380	19.2	17.5	16.2
	323.420	22.4	20.9	19.7
	553.020	23.7	22.9	22.1
	2112.320	1.5	1.9	2.1
	2153.200	3.0	3.7	4.1
	2220.130	4.3	5.3	6.0
	2311.370	5.4	6.7	7.6
	2424.890	6.2	7.8	9.0



**Lower-Energy-Level Populations (in Percent) as a Function of Temperature (continued)**

Element	Energy Level (cm <sup>-1</sup> )	Percent Population at Temperature (°C)		
		2000	2500	3000
Yttrium	0.0	49.3	47.2	45.4
	530.360	50.5	52.2	52.8
Zinc	0.0	100.0	100.0	100.0
Zirconium	0.0	34.2	29.1	25.1
	570.410	31.7	29.3	26.7
	1240.840	25.2	25.6	24.9
	4186.110	1.7	2.6	3.4
	4196.850	0.3	0.5	0.7
	4376.280	0.9	1.4	1.8
	4870.530	0.6	1.1	1.5
	5023.410	0.9	1.6	2.3
	5101.680	0.9	1.5	2.2
	5249.070	1.1	2.0	2.8
	5540.540	1.1	2.2	3.2
	5888.930	1.1	2.2	3.3
	8057.300	0.2	0.5	1.0

*Note:* These data were taken from Reference 12.

## CRITICAL OPTIMIZATION PARAMETERS FOR AES/AAS METHODS

In most multiparameter instrumental techniques, the parameters can be classified into two types: independent and dependent. Independent parameters can be optimized independently from all other parameters and can therefore be subjected to a univariate approach; i.e., the variable can be adjusted until the largest signal-to-noise ratio (SNR) is obtained and set at that value for the best instrumental performance. This is the simplest situation and can be handled in a very straightforward manner.

Dependent parameters are an entirely different matter. Most dependent parameters have optimum values that depend on the value of the other parameters. If the value of any variable is changed, then the optimum for the parameter under question will be different.

The following table lists the parameters for FAAS, EAAS, and FAES, which are both dependent and independent. A “yes” in any column indicates that the listed parameter is appropriate for that technique. If an optimization is necessary when independent parameters are involved, it is important to use a systematic approach that permits one to vary all parameter values to develop the optimum for each. If the variables are simply varied one at a time, false optimum values and poor results will be obtained. Experimental design techniques are required for good results; one of the best approaches is the SIMPLEX technique, which has been fully discussed in the literature.<sup>15</sup>

**Independent Parameters**

Parameter	FAAS	EAAS	FAES
Excitation source power	Yes	Yes	na <sup>a</sup>
Photomultiplier voltage <sup>b</sup>	Yes	Yes	Yes
Readout gain <sup>c</sup>	Yes	Yes	Yes
Noise suppression setting <sup>d</sup>	Yes	Yes	Yes

**Dependent (Interdependent) Parameters**

Parameter	FAAS	EAAS	FAES
Oxidant gas flow rate	Yes	na	Yes
Fuel-to-oxidant ratio	Yes	na	Yes
Sheath gas flow rate <sup>e</sup>	Yes	Yes	Yes
Solution flow rate <sup>f</sup>	Yes	na	Yes
Sample size	na	Yes	na
Height of optical measurement	Yes	Yes	Yes
Monochromator slit setting	Yes	Yes	Yes
Burner variables <sup>g</sup>	Yes	na	Yes
Furnace variables <sup>h</sup>	na	Yes	na

*Note:* This information was taken from reference 16.

<sup>a</sup> na = not applicable.

<sup>b</sup> The photomultiplier tube voltage does not affect the SNR unless extreme voltages are used. It will specify the level of signal that is observed.

<sup>c</sup> The gain does not affect the SNR until electronic noise becomes important. It also specifies the level of signal that is observed.

<sup>d</sup> This specifies the frequency response of the system and is accompanied by a time requirement. More noise filtering requires a long measurement.

<sup>e</sup> Most commercial burners do not use a sheath gas; however, there is always the possibility of a sheath gas in EAAS.

<sup>f</sup> This is important if the sample solution flow rate is controlled by a pump rather than by the oxidant gas flow rate.

<sup>g</sup> Some burners have additional variables such as bead position and nebulizer position.

<sup>h</sup> The timing cycle and temperature are always critical variables for the graphite furnaces.

### Flame Temperatures and References on Temperature Measurements

Flame Type	Experimental Measurement Range (K)	Calculated Stoichiometric Temperature (K)	Typical <sup>a</sup> (K)
Hydrocarbon/air	1900–2150	2228	2000
Acetylene/air	2360–2600	2523	2450
Acetylene/nitrous oxide	2830–3070	3148	2950
Hydrogen/air	2100–2300	2373	2300
Hydrogen/oxygen	2500–2900	3100	2800
Acetylene/oxygen	2900–3300	3320	3100

*Note:* These data were taken from Reference 2.

<sup>a</sup> This value represents the value most often cited for flames used in analytical spectroscopy.

### REFERENCES THAT DISCUSS THE TECHNIQUES OF TEMPERATURE MEASUREMENT

- Gaydon, A.G. and Wolfhard, H.G., *Flames, Their Structure, Radiation, and Temperature*, Chapman & Hall Ltd., London, 1970.
- Fristrom, R.M. and Westenberg, A.A., *Flame Structure*, McGraw-Hill, New York, 1965.
- Tourin, R.H., *Spectroscopic Gas Temperature Measurement*, Elsevier Publishing Co., Amsterdam, 1966.
- Gaydon, A.G. and Wolfhard, H.G., The spectrum-line reversal method of measuring flame temperature, *Proc. Phys. Soc. (London)*, 65A, 19, 1954.
- Browner, R.F. and Winefordner, J.D., Measurement of flame temperatures by a two-line atomic absorption method, *Anal. Chem.*, 44, 247, 1972.
- Omenetto, N., Benetti, P., and Rossi, G., Flame temperature measurements by means of atomic fluorescence spectrometry, *Spectrochim. Acta*, 27B, 253, 1972.
- Herzfield, C.M., *Temperature, Its Measurement and Control in Science and Industry*, Part 2, Vol. III, Dahl, I. Ed., Reinhold, New York, 1962.
- Alkemade, C.Th.J., Hollander, T.J., Snelleman, W., and Zeegers, P.J.Th., *Metal Vapours in Flames*, Pergamon Press, New York, 1982.

## FUNDAMENTAL DATA FOR THE COMMON TRANSITIONS

To the extent possible, the fundamental data for the transition commonly used with the methods discussed in this section are given in this table. The transition in nm; the type of transition (I indicates atomic and II indicates ionic); the lower and upper energy levels, E-low and E-high, in  $\text{cm}^{-1}$ ; the statistical weight,  $g(i)$ , of the lower level (i); the transition probability,  $A(ji)$ , in  $\text{sec}^{-1}$ ; and the merit and reference for the transition probability are listed. In some cases,  $g(i)$  and  $A(ji)$  were only available in the multiplied form, and in these cases, the  $gA = xx$  format was used. If a blank appears, no information was available for that specific column.

**Fundamental Data for the Common Transitions**

Element	Symbol	Wavelength (nm)	Type	E-low ( $\text{cm}^{-1}$ )	E-high ( $\text{cm}^{-1}$ )	$g(i)$	$A(ji)$ , $10^5 \text{ sec}^{-1}$	Merit <sup>a</sup>	Reference
Aluminum	Al	167.0787	II	0	32,435	4	0.63	C	3
		308.2153	I	112	32,437	6	0.73	C	3
		309.2710	I	112	25,348	2	0.98	C	3
		396.1520	I						
Antimony	Sb	206.833	I	0	48,332	6	42	E	2
		217.581	I	0	45,945	4	13.8	E	2
		231.147	I	0	43,249	2	3.75	E	2
		259.805	I	8512	46,991	2	32	E	2
Arsenic	As	189.042	I	0	52,898	6	2.0	D	3
		193.759	I	0	51,610	4	2.0	D	3
		197.262	I	10,592	50,694	2	2.0	D	3
		234.984	I	18,186	53,136	4	3.1	D	3
		286.044	I		53,136	2	0.55	D	3
Barium	Ba	455.403	II	0	21,952	4	1.17	A	3
		493.409	II	0	20,262	2	0.955	B	3
		553.548	I	0	18,080	3	1.15	B	3
Beryllium	Be	234.861	I	0	42,565	3	5.56	B	3
		313.042	II	0	31,935	4	1.14	B	3
		313.107	II	0	31,929	2	1.15	B	3
Bismuth	Bi	223.061	I	0	44,817	4	0.25	D	3
		289.798	I	11,418	45,916	2	1.53	C	3
Boron	B	208.891	I	0	47,857	4	0.28	D	3
		208.957	I	16	47,857	6	0.33	D	3
		249.677	I	0	40,040	2	0.84	C	3
		249.773	I	16	40,040	2	1.69	C	3
Bromine	Br	470.486	II		115,176	7	1.1	D	3
		827.244	I						
Cadmium	Cd	214.441	II	0	46,619	4	2.8	C	3
		226.502	II	0	44,136	2	3.0	C	3
		228.8022	I	0	43,692	3	0.24	D	3
		326.1055	I	0	30,656	3	0.004	C	3
Calcium	Ca	364.441	I	15,316	42,747	7	0.355	C	3
		393.366	II	0	25,414	4	1.47	C	3
		396.847	II	0	25,192	2	1.4	C	3
		422.673	I	0	23,652	3	2.18	B	3
Carbon	C	193.0905	I	21,648	61,982	3	3.7	D	3
		247.856	I		61,982	3	0.18	D	3
Cerium	Ce	394.275	II	6913	32,269	$gA = 19$		E	2
		413.765	II	4166	28,327	$gA = 4.8$		E	2
		418.660	II	6968	30,847	$gA = 18$		E	2
Cesium	Cs	455.5276	I	0	21,946	4	0.019	C	3
		852.1122	I	0	11,732	4	0.32	E	2
Chlorine	Cl	413.250	II		153,259	5	1.6	D	3
		837.594	I						

Fundamental Data for the Common Transitions (continued)

Element	Symbol	Wavelength (nm)	Type	E-low (cm <sup>-1</sup> )	E-high (cm <sup>-1</sup> )	g(i)	A(ji), 10 <sup>5</sup> sec <sup>-1</sup>	Merit <sup>a</sup>	Reference
Chromium	Cr	205.552	II	0	48,632	gA = 9.1		E	2
		267.716	II	12,304	49,646	gA = 132		E	2
		357.869	I	0	27,935	gA = 8.3		E	2
		425.435	I	0	23,499	9	0.315	B	3
Cobalt	Co	228.615	II	3350	47,078	gA = 169		E	2
		238.892	II	3350	45,198	ga = 278		E	2
		240.725	I	0	41,529	12 3.08		E	2
		352.685	I	0	28,346	10 0.12		C	3
Copper	Cu	213.5981	II	0	30,784	4	1.39	B	3
		324.754	I	0	30,784	4	1.39	B	3
		327.396	I	0	30,535	2	1.37	B	3
Dysprosium	Dy	353.170	II	0	28,307	gA = 19		E	2
		404.597	I	0	24,709	15 1.5		D	3
		421.172	I	0	23,737	19 2.08		C	3
Erbium	Er	337.271	II	0	29,641	gA = 13		E	2
		400.796	I	0	24,943	15 26		D	3
Europium	Eu	381.967	II	0	26,173	gA = 4.8		E	2
		459.403	I	0	21,761	10 1.4		D	3
Fluorine	F	685.603	I		116,987	8	0.42	D	3
Gadolinium	Gd	342.247	II	1935	31,146	gA = 19		E	2
		368.413	I	0	27,136	gA = 12		E	2
		440.186	I	1719	24,430	gA = 4.2		E	2
Gallium	Ga	287.424	I	0	34,782	4	1.2	C	3
		294.364	I	826	34,788	6	1.4	C	3
		417.204	I	826	24,789	2	0.92	C	3
Germanium	Ge	199.8887	I	1410	51,438	5	0.55	C	3
		209.4258	I	1410	49,144	7	0.97	C	3
		265.1172	I	1410	39,118	5	2.0	C	3
Gold	Au	242.795	I	0	41,174	4	1.5	D	3
		267.595	I	0	37,359	2	1.1	D	3
Hafnium	Hf	277.336	II	6344	42,391	gA = 14		E	2
		307.288	I	0	32,533	gA = 3.2		E	2
		339.980	II	0	29,405	gA = 1.1		E	2
Holmium	Ho	345.600	II	637	26,331				
		389.102	II	0	24,660				
		405.393	I	0	24,361				
		410.384	I						
Hydrogen	H	486.133	I	82,259	102,824	32	0.084	A	17
		656.2852	I	82,259	97,492	18	0.441	A	17
Indium	In	230.605	II	0	43,349	gA = 0.032		E	2
		303.936	I	0	32,892	gA = 7.1		E	2
		325.609	I	2213	32,915	6	1.3	D	3
		451.131	I	2213	24,373	2	1.02	C	3
Iodine	I	183.038	I		56,093	4	2.71	C	3
		206.163	I						
Iridium	Ir	208.882	I	0	47,858	12	28	E	2
		224.268	II	0	44,576	10	0.56	E	2
		263.971	I	0	37,872				
Iron	Fe	238.204	II	0	41,968	gA = 92		E	2
		248.3271	I	0	40,257	11	4.9	C	3
		259.9396	II	0	38,459	10	2.22	C	3
		371.9935	I	0	26,875	11	0.163	B	3
Lanthanum	La	333.749	II	3250	33,204	gA = 3.5		E	2
		408.672	II	0	24,463	5	0.20	E	2
		550.134	I	0	18,172	4	0.08	E	2

Fundamental Data for the Common Transitions (continued)

Element	Symbol	Wavelength (nm)	Type	E-low (cm <sup>-1</sup> )	E-high (cm <sup>-1</sup> )	g(i)	A(ji), 10 <sup>5</sup> sec <sup>-1</sup>	Merit <sup>a</sup>	Reference
Lead	Pb	217.000	I	0	46,068	3	1.5	D	3
		220.3534	II	14,081	59,448	gA = 5.7		E	2
		283.3053	I	0	35,287	3	0.58	D	3
		368.3462	I	7819	34,960	1	1.5	D	3
Lithium	Li	670.776	I	0	1494	4	0.372	B	3
Lutetium	Lu	261.545	II	0	38,223	gA = 5.8		E	2
		451.857	I	0	22,125	4	0.21	B	3
Magnesium	Mg	279.553	II	0	35,761	4	4.0	C	3
		280.270	II	0	35,669	2	2.6	C	3
		285.213	I	0	35,051	3	5.3	D	3
Manganese	Mn	257.610	II	0	38,807	9	8.89	E	2
		279.482	I	0	35,770	8	3.7	C	3
		403.076	I	0	24,802	8	0.19	C	3
Mercury	Hg	184.905	II	0	39,412	3	0.13	D	3
		194.227	II						
		253.652	I						
Molybdenum	Mo	202.030	II	0	49,481	gA = 24		E	2
		313.259	I	0	31,913	9	1.09	E	2
		379.825	I	0	26,321	9	0.49	E	2
		390.296	I	0	25,614	5	0.42	E	2
Neodymium	Nd	401.225	II	5086	30,002	20	0.55	D	3
		463.424	I	0	21,572	gA = 2.0		E	2
		492.453	I	0	20,301	gA = 2.0		E	2
Nickel	Ni	221.648	II	0	53,496	12	5.5	D	3
		232.003	I	205	43,090	11	6.9	C	3
		352.454	I		28,569	5	1.0	C	3
Niobium	Nb	309.418	II	4146	36,455	13	1.1	E	2
		334.906	I	2154	32,005	10	0.45	E	2
		405.894	I	1050	25,680	12	0.65	E	2
Nitrogen	N	174.2729	I						
		821.634	I						
Osmium	Os	225.585	II	0	44,315	11	1.0	E	2
		290.906	I	0	34,365	9	0.034	E	2
		442.047	I	0	22,616				
Oxygen	O	436.825	I		86,631	7	0.34	B	3
		777.194	I						
Palladium	Pd	244.791	I	0	40,839	3	0.28	E	2
		247.642	I	0	40,369	3	0.37	E	2
		340.458	I	6564	35,928	9	1.33	E	2
		363.470	I	6564	34,069	5	1.24	E	2
Phosphorus	P	177.499	I	0	56,340	6	2.17	C	3
		213.547	I	11,362	58,174	4	0.211	C	3
		253.561	I	18,748	58,174	4	0.20	C	3
Platinum	Pt	214.423	I	0	46,622	7	5.14	E	2
		265.945	I	0	37,591	9	0.91	E	2
Potassium	K	766.490	I	0	13,043	4	0.387	B	3
Praseodymium	Pr	390.805	II	0	23,660	gA = 1.4		E	2
		422.535	II	0	20,190				
		495.137	I						
Rhenium	Re	197.3	II	0	45,148	gA = 15		E	2
		221.426	I	0	28,890				
		346.046							
Rhodium	Rh	233.477	II	16,885	59,702	gA = 44		E	2
		343.489	I	0	29,105	12	0.34	E	2
		369.236	I	0	27,075	8	0.35	E	2

Fundamental Data for the Common Transitions (continued)

Element	Symbol	Wavelength (nm)	Type	E-low (cm <sup>-1</sup> )	E-high (cm <sup>-1</sup> )	g(i)	A(ji), 10 <sup>5</sup> sec <sup>-1</sup>	Merit <sup>a</sup>	Reference
Rubidium	Rb	420.180	I	0	23,793	4	0.018	C	3
		780.027	I	0	12,817	4	0.370	B	3
Ruthenium	Ru	240.272	II	9152	50,758	gA = 247		E	2
		349.894	I	0	28,572	13	0.46	E	2
		372.803	I	0	26,816	11	0.42	E	2
Samarium	Sm	359.260	II	3053	30,880	gA = 6.3		E	2
		373.912	II	326	27,063	gA = 21		E	2
		429.674	I	4021	27,288	gA = 3.3		E	2
		476.027	I	812	21,813				
Scandium	Sc	361.384	II	178	27,841	9	0.14	D	3
		391.181	I	168	25,725	8	1.37	C	3
Selenium	Se	196.09	I	0	50,997	2	100	E	2
		203.98	I	1989	50,997	2	65	E	2
Silicon	Si	251.6113	I	223	39,955	5	1.21	C	3
		288.1579	I	6299	40,992	3	1.89	C	3
Silver	Ag	328.068	I	0	30,473	4	1.4	B	3
		338.2068	I	0	29,552	2	1.3	B	3
Sodium	Na	330.237	I	0	30,273	4	0.028	C	3
		588.9950	I	0	16,973	4	0.622	A	3
		589.5924	I	0	16,956	2	0.618	A	3
Strontium	Sr	407.771	II	0	24,517	4	1.42	C	3
		421.552	II	0	23,715	2	1.27	C	3
		460.733	I	0	21,698	3	2.01	B	3
Sulfur	S	180.7311	I		55,331	3	3.8	C	3
		182.0343	I		55,331	3	2.2	C	3
		216.89							
Tantalum	Ta	226.230	II	2642	46,831	gA = 35		E	2
		240.063	II	6187	47,830	gA = 516		E	2
		271.467	I	0	36,826	6	1.17	E	2
		296.513	II	0	33,715	gA = 7.8		E	2
		474.016	I	9976	31,066	4	0.028	E	2
Tellurium	Te	214.281	I	0	46,653	3	38	E	2
		238.578	I	4751	46,653	3	5.47	E	2
Terbium	Tb	350.917	II	0	28,488	gA = 7.2		E	2
		367.635	II	1016	28,209				
		432.643	I	0	23,107				
Thallium	Tl	190.864	II	0	36,118	4	1.26	C	3
		276.787	I	0	26,478	2	0.625	B	3
		377.572	I	7793	26,478	2	0.705	B	3
		535.046	I						
Thorium	Th	283.7295	II	6214	41,448	gA = 0.12		E	2
		324.4448	I	0	30,813	gA = 0.66		E	2
		401.9129	II	0	24,874	gA = 0.08		E	2
		491.9816	II	6168	26,489				
Thulium	Tm	313.126	II	0	31,927	gA = 4.6		E	2
		346.220	II	0	28,875	gA = 2.5		E	2
		371.791	I	0	26,889	gA = 8.3		E	2
Tin	Sn	189.991	II	0	44,509	3	1.6	D	3
		224.605	I	1692	44,145	5	1.7	D	3
		235.484	I	3428	38,629	5	1.7	D	3
		283.999	I	8613	39,257	3	2.7	D	3
		326.234	I						
Titanium	Ti	334.941	II	393	30,241	12	1.3	D	3
		364.268	I	170	27,615	9	0.67	C	3
		365.350	I	387	27,750	11	0.66	C	3
		368.520	II	4898	32,026				

Fundamental Data for the Common Transitions (continued)

Element	Symbol	Wavelength (nm)	Type	E-low (cm <sup>-1</sup> )	E-high (cm <sup>-1</sup> )	g(i)	A(ji), 10 <sup>5</sup> sec <sup>-1</sup>	Merit <sup>a</sup>	Reference
Tungsten	W	207.911	II	6147	54,229	gA = 93		E	2
		255.135	I	0	39,183	7	1.17	E	2
		276.427	II	0	36,165	gA = 6.9		E	2
		400.875	I	2951	27,890	9	0.20	E	2
Uranium	U	263.553	II	0	27,887	15	0.10	B	3
		358.488	I	289	26,191	gA = 2.6		E	2
		385.957	II	0	16,900	gA = 0.12		E	2
		591.539	I						
Vanadium	V	309.311	II	3163	35,483	13	1.8	D	3
		311.062	II	2809	34,947	9	1.5	D	3
		318.540	I	553	31,937	12	1.4	D	3
		437.924	I	2425	25,254	12	1.2	D	3
Ytterbium	Yb	328.937	II	0	30,392	4	1.8	C	3
		369.419	II	0	27,062	2	1.4	C	3
		398.799	I	0	25,068	3	1.76	C	3
Yttrium	Y	362.094	I	530	28,140	4	1.55	E	2
		371.030	II	1450	28,394	8	0.64	E	2
		377.433	II	1045	27,532				
		410.238	I	530	24,900				
Zinc	Zn	202.548	II	0	49,355	4	3.3	C	3
		213.856	I	0	46,745	3	7.09	B	3
Zirconium	Zr	343.823	II	763	29,840	gA = 13		E	2
		351.960	I	0	28,404	7	0.71	E	2
		360.119	I	1241	29,002	11	0.91	E	2

<sup>a</sup> The key for the merit of the A(ji) values follows that given in Reference 3: A = within 3%; B = within 10%; C = within 25%; D = within 50%; E = greater than 50%.



## ACTIVATED CARBON AS A TRAPPING SORBENT FOR TRACE METALS

Activated carbon is commonly used to preconcentrate samples of heavy metals before spectrometric analysis.<sup>1</sup> This material is typically used by passing the sample through a thin layer (50 to 150 mg) of the activated carbon that is supported on a filter disk. It can also be used by shaking 50 to 150 mg of activated carbon in the solution containing the heavy metal and then filtering the sorbent out of the solution.

## REFERENCES

1. Alfasi, Z.B. and Wai, C.M., *Preconcentration Techniques for Trace Elements*, CRC Press, Boca Raton, FL, 1992.

**Activated Carbon as a Trapping Sorbent for Trace Metals**

Matrices	Trace Metals	Complexing Agents	Determination Methods
Water	Ag, Bi, Cd, Co, Cu, Fe, In, Mg, Mn, Ni, Pb, Zn	(NaOH; pH 7–8)	AAS
Water	Ag, As, Ca, Cd, Ce, Co, Cu, Dy, Fe, La, Mg, Mn, Nb, Nd, Ni, Pb, Pr, Sb, Sc, Sn, U, V, Y, Zn	8-Quinololinol	SSMS, XRF
Water	Ba, Co, Cs, Eu, Mn, Zn	APDC, DDTC, PAN, 8-Quinololinol	XRF
Water	Hg, methyl mercury	—	AAS
Water	Hg (halide)	—	AAS
Water	Hg (halide)	—	AAS
Water	U	L-Ascorbic acid	INAA
HNO <sub>3</sub> , water, Al, KCl	Ag, Bi, Cd, Cu, Hg, Pb, Zn	Dithizone	AAS
Mn, MnO <sub>3</sub> , Mn salts	Bi, Cd, Co, Cu, Fe, In, Ni, Pb, Tl, Zn	Ethyl xanthate	AAS
Co, Co(NO <sub>3</sub> ) <sub>2</sub>	Ag, Bi	APDC	AAS
Ni, Ni(NO <sub>3</sub> ) <sub>2</sub>	Ag, Bi	APDC	AAS
Mg, Mg(NO <sub>3</sub> ) <sub>2</sub>	Ag, Cu, Fe, Hg, In, Mn, Pb, Zn	(pH 8.1–9)	AAS
Al	Cd, Co, Cu, Ni, Pb	Thioacetamide	AAS
Ag, TINO <sub>3</sub>	Bi, Co, CU, Fe, In, Pb	Xenol orange	AAS
Cr salts	Ag, Bi, Cd, Co, Cu, In, Ni, Pb, Tl, Zn	HAHDTC	AAS
Co, In, Pb, Ni, Zn	Ag, Bi, Cu, Tl	DDTC	AAS
Se	Cd, Co, Cu, Fe, Ni, Pb, Zn	DDTC	AAS
NaClO <sub>4</sub>	Ag, Bi, Cd, Co, Cu, Fe, Hg, In, Mn, Ni, Pb	(pH 6)	AAS

*Note:* APDC = ammonium pyrrolidinedicarbodithioate; DDTC = diethyldithiocarbamate; HAHDTC = hexamethyleneammonium hexaethylenedithiocarbamate; PAN = 1-(2-pyridylazo)-2-naphthol.

## REAGENT-IMPREGNATED RESINS AS TRAPPING SORBENTS FOR TRACE MINERALS

Reagent-impregnated resins can be used as trapping sorbents for the preconcentration of heavy metals.<sup>1</sup> These materials can be used in the same way as activated carbons.

### REFERENCES

1. Alfasi, Z.B. and Wai, C.M., *Preconcentration Techniques for Trace Elements*, CRC Press, Boca Raton, FL, 1992.

**Reagent-Impregnated Resins as Trapping Sorbents for Trace Minerals**

Reagents	Adsorbents	Metals
TBP	Porous polystyrene DVB resins	U
YBP	Levextrel (polystyrene DVB resins)	U
DEHPA	Levextrel	Zn
DEHPA	XAD-2	Zn
Alamine 336	XAD-2	U
LIX-63	XAD-2	Co, Cu, Fe, Ni, etc.
LIX-64N, -65N	XAD-2	Cu
Hydroxyoximes	XAD-2	Cu
Kelex 100	XAD-2	Co, Cu, Fe, Ni
Kelex 100	XAD-2,4,7,8,11	Cu
Dithizone, STTA	Polystyrene DVB resins	Hg
Dithizone (acetone)	XAD-1,2,4,7,8	Hg, methyl mercury
DMABR	XAD-4	Au
Pyrocatechol violet	XAD-2	In, Pb
TPTZ	XAD-2	Co, Cu, Fe, Ni, Zn

*Note:* TBP = tributyl phosphate; DEHPA = diethylhexyl phosphoric acid; STTA = monothio-thenolytrifluoroacetone; DMABR = 5-(4-dimethylaminobenzylidene) rhodanine; TPTZ = 2,4,6-tri(2-pyridyl) 1,3,5-triazine; LIX-63 = aliphatic  $\alpha$ -hydroxyoxime; LIX-65N = 2-hydroxy-5-nonylbenzophenoneoxime; LIX-64N = a mixture of LIX-65N with approximately 1% (vol/vol) of LIX-63.

## REAGENT-IMPREGNATED FOAMS AS TRAPPING SORBENTS FOR INORGANIC SPECIES

Reagent-impregnated foams can be used as trapping sorbents for the preconcentration of heavy metals.<sup>1</sup> These materials can be used in the same way as activated carbons.

### REFERENCES

1. Alfasi, Z.B. and Wai, C.M., *Preconcentration Techniques for Trace Elements*, CRC Press, Boca Raton, FL, 1992.

**Reagent-Impregnated Foams as Trapping Sorbents for Inorganic Species**

Matrices	Elements	Concentration	Foam Type	Reagents	Determination Methods
Water Natural water	<sup>131</sup> I, <sup>203</sup> Hg	Traces	Polyether	Alamine 336	Radiometry
Water	Bi, Cd, Co, Cu, Fe, Hg, Ni, Pb, Sn, Zn	Traces	Polyether	Amberlite LA-2	Spectroph., AAS
Water	Co, Fe, Mn	Traces µg/L	Polyether	PAN	Radiometry
Natural water	Cd	µg/L	Polyether	PAN	AAS
Water	Au, Hg	µg/L	Polyether	PAN	NAA
Water	Ni	Traces to µg/L	—	DMG, α-benzylidioxime	Spectroph., AAS
Water	Cr	µg/L	Polyether	DPC	Colorimetry
Water	Hg, methyl-Hg, phenyl-Hg	µg/L	Polyether	DADTC	Radiometry
Natural water	Sn	Traces	Polyether	Toluene-3,4-dithiol	Spectroph.
Water	Cd, Co, Fe, Ni	Traces	Polyether	Aliquot	Spectroph.
Water	Th	Traces	Polyether	PMBP	Radiometry
Water	PO <sub>4</sub> <sup>3-</sup>	Traces		HDEHP–TBP Amine–molybdate–TBP	Spectroph. Colorimetry

*Note:* PAN = 1-(2-pyridylazo)-2-naphthol; DMG = dimethylglyoxime; DPC = 1,5-diphenylcarbazide; DADTC = diethylammonium diethyldithiocarbamate; PMBP = 1-phenyl-3-methyl-4-benzoyl-pyrazolone-5; HDEHP = bis-[2-ethylhexyl]phosphate; TBP = tributyl phosphate; Spectroph. = spectrophotometry; AAS = atomic absorption spectrometry; NAA = neutron activation analysis.

## CHAPTER 12

# Qualitative Tests

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Organic Group Qualitative Tests  
Protocol for Chemical Tests  
Organic Families and Chemical Tests  
Inorganic Group Qualitative Tests  
Tests for Anions  
Tests for Cations  
Organic Precipitation Reagents for Inorganic Ions

## ORGANIC GROUP QUALITATIVE TESTS

The following flowcharts and notes provide a step-by-step process for the identification of functional groups that may be present in an unknown sample.<sup>1-11</sup> These are meant to augment and confirm information obtainable using instrumental methods of analysis. It will usually be necessary to use gas or liquid chromatography before these wet chemical tests to determine the number of components present in a given sample. Since many of these tests require the use of sometimes toxic compounds, the strictest rules of laboratory safety must be observed at all times. The use of a fume hood is often required. The book by Feigl et al.<sup>11</sup> is an excellent guide for spot tests.

## REFERENCES

1. Pasto, D.J. and Johnson, C.R., *Laboratory Text for Organic Chemistry*, Prentice Hall, Englewood Cliffs, NJ, 1979.
2. Svoronos, P., Sarlo, E., and Kulawiec, R., *Experiments in Organic Chemistry*, McGraw-Hill, Dubuque, IA, 1997.
3. Roberts, R.M., Gilbert, J.C., Rodewald, L.B., and Wingrove, A.S., *Modern Experimental Organic Chemistry*, Saunders, New York, 1985.
4. Hodgman, C.D., Weast, R.C., and Selby, S.M., *Tables for Identification of Organic Compounds*, Chemical Rubber Publishing Co., Cleveland, 1950.
5. Kamm, O., *Qualitative Organic Analysis*, John Wiley & Sons, New York, 1932.
6. Vogel, A.I., Furniss, B.S., and Tatchell, A.R., *Vogel's Textbook of Practical Organic Chemistry*, John Wiley & Sons, New York, 1989.
7. Shriner, R.L., Hermann, C.K.F., Morrill, T.C., Fuson, R.C., and D.Y. Curtin, *The Systematic Identification of Organic Compounds, A Laboratory Manual*, John Wiley & Sons, New York, 1998.
8. Vogel, A.I., *Elementary Practical Organic Chemistry*, Part 2, John Wiley & Sons, New York, 1966.
9. Behforouz, M., Getting the acid out of your 2,4-DNPH, *J. Chem. Educ.*, 63, 723, 1986.
10. Durst, H.D. and Gokel, G.W., *Experimental Organic Chemistry*, McGraw-Hill, New York, 1987.
11. Feigl, F., Anger, V., and Oesper, R.E., *Spot Tests in Organic Analysis*, Elsevier, Amsterdam, 1966.

## PROTOCOL FOR CHEMICAL TESTS

The following section gives a suggested protocol for the chemical tests used in the identification of organic compounds. Variations of the procedures are possible, but these protocols have been used successfully for most organic identifications.<sup>1-10</sup>

## REFERENCES

1. Vogel, A.I., Furniss, B.S., and Tatchell, A.R., *Vogel's Textbook of Practical Organic Chemistry*, John Wiley & Sons, New York, 1989.
2. Shriner, R.L., Hermann, C.K.F., Morrill, T.C., Fuson, R.C., and D.Y. Curtin, *The Systematic Identification of Organic Compounds, A Laboratory Manual*, John Wiley & Sons, New York, 1998.
3. Vogel, A.I., *Elementary Practical Organic Chemistry*, Part 2, John Wiley & Sons, New York, 1966.
4. Pasto, D.J. and Johnson, C.R., *Laboratory Text for Organic Chemistry*, Prentice Hall, Englewood Cliffs, NJ, 1979.
5. Roberts, R.M., Gilbert, J.C., Rodewald, L.B., and Wingrove, A.S., *Modern Experimental Organic Chemistry*, Saunders, New York, 1985.
6. Uamm, O., *Qualitative Organic Analysis*, John Wiley & Sons, New York, 1932.
7. Behforout, M., Getting the acid out of your 2,4-DNP, *J. Chem. Educ.*, 63, 723, 1986.
8. Durst, H.D. and Gokel, G.W., *Experimental Organic Chemistry*, McGraw-Hill, New York, 1987.
9. Fieser, L.F. and Freser, M., *Reagents for Organic Synthesis*, John Wiley & Sons, New York, 1968.
10. Svoronos, P., Sarlo, E., and Kulawiec, R., *Experiments in Organic Chemistry*, McGraw-Hill, Dubuque, IA, 1997.

**Aluminum chloride–chloroform** To a mixture of 2 ml of chloroform and 0.2 to 0.4 dry aluminum chloride in a test tube add 5 to 10 drops of your unknown aromatic compound. A color formation will indicate the presence of a benzene ring.

**Basic hydrolysis** Reflux 0.1 g of the compound in 5 ml of a 10% sodium hydroxide solution.

**Benedict's reagent** Add 5 to 10 drops of your unknown to 1 to 2 ml of the Benedict's reagent and heat. A positive test will change the blue copper (II) color of the reagent and subsequent precipitation of the red copper (I) oxide.

**Bromine test** The compound to be tested is treated with a few drops of 1 to 5% Br<sub>2</sub>/CCl<sub>4</sub> solution. A positive test is indicated by decolorization of the bromine color.

**Ceric ammonium nitrate** To 1 to 2 ml of 5% ceric ammonium nitrate add 10 drops of the compound to be tested. A change to an orange/red color is indicative of an alcohol (detection limit, 100 mg; compounds tested, C<sub>1</sub> to C<sub>10</sub>).

**Dichromate test** Add 10 drops of the alcohol to be tested to a mixture of 1 ml of 1% Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and 5 drops of concentrated H<sub>2</sub>SO<sub>4</sub>. A blue-green solution is a positive test for a 1 or 2° alcohol. Three degree alcohols do not react, and therefore, the solution stays orange (detection limit, 20 µg; compounds tested, C<sub>1</sub> to C<sub>8</sub>). Slight heating may be necessary for water-immiscible alcohols. Extensive heat gives a positive test also for tertiary alcohols, which is due to the water elimination of the alcohol and oxidation of the formed alkene.

**2,4-Dinitrophenylhydrazine test (2,4-DNP)** Add 10 drops of the compound to be tested to 1 ml of the 2,4-DNP reagent. A yellow to orange-red precipitate is considered a positive test. The crystals can be purified by washing them with 5% NaHCO<sub>3</sub>, then with water, and finally recrystallized from ethanol. The 2,4-DNP reagent can be prepared by dissolving 1 g of 2,4-dinitrophenylhydrazine in 5 ml of concentrated H<sub>2</sub>SO<sub>4</sub> and then mixing it with 8 ml of water and 20 ml of 95% ethanol. The solution should be filtered before reacting it with the unknown compound (detection limit, 20 µg; compounds tested, C<sub>1</sub> to C<sub>8</sub>).

**Fehling's test** The test is similar to the Benedict's test (see above).

**Ferric chloride test** Add 10 drops of 3% aqueous FeCl<sub>3</sub> solution to 1 ml of a 5% aqueous (ethanol) solution of the compound in question. Phenols give red, blue, purple, or green colorations. The same test can be done by using chloroform as a solvent (detection limit, 50 µg).

**Hinsberg test** To 0.5 ml of the amine (0.5 g, if solid) in a test tube add 1 ml of benzenesulfonyl chloride and 8 ml of 10% NaOH. Stopper the tube and shake for 3 to 5 min. Remove the stopper and warm the tube while shaking in a hot water bath (70°C) for about 1 min. No reaction is indicative of a 3° amine; the amine becomes soluble upon acidification (pH = 2 to 4) with 10% HCl. If a precipitate is present in the alkaline solution, dilute with 5 to 8 ml of H<sub>2</sub>O and shake. If the precipitate does not dissolve, the original amine is probably a 2° one. If the solution is clear, acidify (pH = 4) with 10% HCl. The formation of a precipitate is indicative of a 1° amine (detection limit, 100 mg; compounds tested, C<sub>1</sub> to C<sub>10</sub>).

**Iodoform test** The reagent calls for the mixture of 10 g of I<sub>2</sub> and 20 g of KI in 100 ml of water. The reagent is then added dropwise to a mixture of 10 drops of the compound in question in 2 ml of water (or dioxane, to facilitate the solubility) and 1 ml of 10% aqueous NaOH solution until a persistent brown color remains (even when heating in a hot water bath at 60°C). A yellow precipitate is indicative of iodoform (CHI<sub>3</sub>) formation and is characteristic of a methyl ketone, acetaldehyde, or alcohol of the general formula CH<sub>3</sub>CH(R)OH (R = alkyl, hydrogen). Aldols, RC(=O)CH<sub>2</sub>CH(OH)R', may also give a positive iodoform test by a retro aldol condensation first yielding RC(=O)CH<sub>3</sub> and RCHO (detection limit, 100 mg). In this case, at least the products should be a methyl ketone or acetaldehyde.

**Lucas test** The reagent is made by dissolving 16 g of anhydrous ZnCl<sub>2</sub> in 10 ml of concentrated hydrochloric acid and cooling to avoid HCl loss. Add 10 to 15 drops of the *anhydrous* alcohol to 2 ml of the reagent. Three degree alcohols form an emulsion that appears as two layers (due to the water-insoluble alkyl halide) almost immediately. Two degree alcohols form this emulsion after 2 to 5 min, while 1° alcohols react after a very long time (if at all). Some secondary alcohols (e.g., isopropyl) may not *visually* form the layers because of the low-boiling alkyl halide, which may evaporate.

**Permanganate test** The compound to be tested is treated with 10 to 15 drops of 1% KMnO<sub>4</sub> solution. A positive test is indicated by the formation of a black (MnO<sub>2</sub>) precipitate.

**Silver nitrate test** The compound to be tested is treated with a few drops of 1% alcoholic silver nitrate. A white precipitate indicates a positive reaction. This could be due to either silver chloride (reaction with a reactive alkyl halide), silver alkynide (reaction with a terminal alkyne), or the silver salt of a carboxylic acid (reaction with a carboxylic acid).

**Sodium fusion test** One hundred milligrams of the compound to be analyzed is mixed with a fresh, tiny piece of sodium metal of the size of a small pea in a 4-in. test tube. The test tube is warmed gently until melting of the sodium metal and decomposition (indicated by charring) of the compound occurs. When it appears that all the volatile material has been decomposed, the test tube is strongly heated until the residue acquires a red color. After 3 min of constant heating, the mixture is left to cool to room temperature, and then a few drops of methanol are added. If no smoke appears, then excess of sodium metal is not present and incomplete conversion of the elements (nitrogen, sulfur, halides) is very likely. Addition of another tiny piece of sodium metal and repetition of the heating process is necessary. If smoke appears, then the red-hot test tube is plunged in a small beaker containing 10 to 15 ml of distilled water and covered with a watch glass or a wire gauze. The test tube might shatter, and therefore, having the small beaker placed inside a larger one is recommended. The contents of the test tube together with the broken glass are ground in a mortar using a pestle and then transferred in the small beaker and heated for a few minutes. The solution is then filtered and divided into two larger portions and one 1-ml part.

**Detection of halogens** To the other larger part add 10% H<sub>2</sub>SO<sub>4</sub> until the solution is acidic. Boil off the solution to one third its volume to secure evaporation of H<sub>2</sub>S and HCN gases. Formation of a precipitate upon addition of 10% AgNO<sub>3</sub> solution is indicative of the presence of a halogen: white for a chloride (which is soluble in 6 M NH<sub>4</sub>OH), pale yellow for a bromide (which is only slightly soluble in 6 M NH<sub>4</sub>OH), and canary yellow for iodide (which is insoluble in 6 M NH<sub>4</sub>OH). Should the color of the precipitate be difficult to provide satisfactory identification of the halogen, proceed as follows: the working solution, which has been acidified with 10% H<sub>2</sub>SO<sub>4</sub> and boiled down, is treated with 4 or 5 drops 0.1 N KMnO<sub>4</sub> solution, with enough oxalic acid added to discharge the color of excess permanganate and 0.5 ml of carbon disulfide. Color formation in the carbon disulfide layer indicates the presence of bromine (red-brown) or iodine (purple). Chlorine's presence cannot be detected by color formation. Should the compound to be tested carry both bromine and iodine,

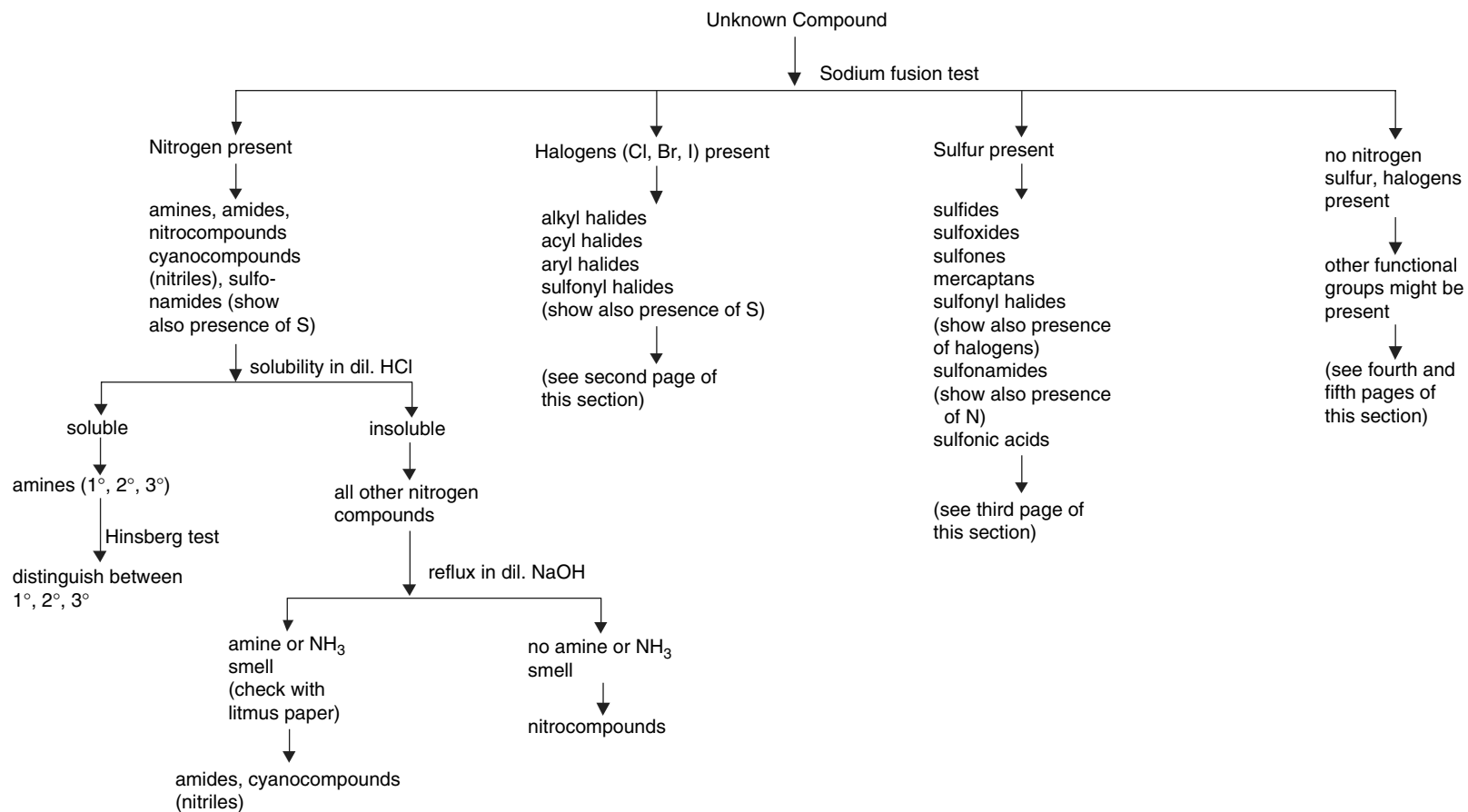
the identification will be insufficient (red-brown to purple carbon disulfide layer). In this case, the addition of a few drops of allyl alcohol decolorizes bromine but does not decolorize iodine.

**Detection of nitrogen** To one of the two larger portions add 10 drops 6 *M* NaOH (pH adjusted to 13), 5 drops of saturated  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ , and 5 drops 30% KF solution. The mixture is then boiled for 30 sec and immediately acidified with 6 *M*  $\text{H}_2\text{SO}_4$ , while stirring until the colloidal iron hydroxides are dissolved. The formation of a blue color is indicative of the presence of nitrogen.

**Detection of sulfur** To the 1-ml part add 10 drops of 6 *M* acetic acid and 2 or 3 drops of 5% lead (II) acetate solution. A black precipitate is indicative of sulfur presence.

**Tollen's test** The reagent should be freshly prepared by mixing two solutions (A and B). Solution A is a 10% aqueous  $\text{AgNO}_3$  solution and solution B is a 10% aqueous NaOH solution. When the test is required, 1 ml of solution A and 1 ml of solution B are mixed, and the silver oxide thus formed is dissolved by dropwise addition of 10% aqueous  $\text{NH}_4\text{OH}$ . To the clear solution, 10 drops of the compound to be tested are added. A silver mirror is indicative of the presence of an aldehyde. The reagent mixture (A + B) is to be prepared immediately prior to use; otherwise, explosive silver fulminate will form. The silver mirror is usually deposited on the walls of the test tube either immediately or after a short warming period in a hot water bath. This is to be disposed of immediately with diluted  $\text{HNO}_3$  (detection limit, 50 mg; compounds tested,  $\text{C}_1$  to  $\text{C}_6$ ).





## ORGANIC FAMILIES AND CHEMICAL TESTS

The following section gives the major organic families and their most important confirmatory chemical tests. This part serves as a complement to the previous section (Organic Group Qualitative Tests).<sup>1-8</sup>

### REFERENCES

1. Pasto, D.J. and Johnson, C.R., *Laboratory Text for Organic Chemistry*, Prentice Hall, Englewood Cliffs, NJ, 1979.
2. Roberts, R.M., Gilbert, J.C., Rodewald, L.B., and Wingrove, A.S., *Modern Experimental Organic Chemistry*, Saunders, New York, 1985.
3. Kamm, O., *Qualitative Organic Analysis*, John Wiley & Sons, New York, 1932.
4. Shriner, R.L., Hermann, C.K.F., Morrill, T.C., Fuson, R.C., and Curtin, D.Y., *The Systematic Identification of Organic Compounds, A Laboratory Manual*, John Wiley & Sons, New York, 1998.
5. Vogel, A.I., *Elementary Practical Organic Chemistry*, Part 2, John Wiley & Sons, New York, 1966.
6. Durst, H.D. and Gokel, G.W., *Experimental Organic Chemistry*, McGraw-Hill, New York, 1987.
7. Fieser, L.F. and Freser, M., *Reagents for Organic Synthesis*, John Wiley & Sons, New York, 1968.
8. Svoronos, P., Sarlo, E., and Kulawiec, R., *Experiments in Organic Chemistry*, McGraw-Hill, Dubuque, IA, 1997.

### Organic Families and Chemical Tests

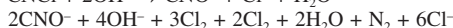
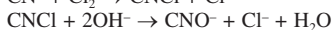
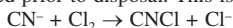
Family	Test	Notes
Alcohols	Ceric ammonium nitrate Dichromate test Iodoform test Lucas test	Positive for all alcohols Positive for 1° and 2° alcohols; negative for 3° alcohols Positive for all alcohols of the general formula $\text{CH}_3\text{CH}(\text{OH})\text{R}$ Immediate reaction for 3°, allylic or benzylic alcohols; slower reaction (2–5 min) for 2°; no reaction for 1° alcohols
Aldehydes	Benedict's test Dichromate test 2,4-Dinitrophenylhydrazine (2,4-DNP) Fehling test Iodoform test Oxime Permanganate test Semicarbazone Tollen's test	Positive for all aldehydes Positive for all aldehydes Positive for all aldehydes (and ketones) Positive for all aldehydes Positive only for acetaldehyde Positive for all aldehydes (and ketones) Positive for all aldehydes Positive for all aldehydes (and ketones) Positive for all aldehydes
Alkanes	No test	
Alkenes	Bromine test Permanganate test Solubility in conc. sulfuric acid	Positive for all alkenes Positive for all alkenes All alkenes dissolve
Alkynes	Bromine test Permanganate test Silver nitrate Sodium metal addition Sulfuric acid	Positive for all alkynes Positive for all alkynes Positive for all terminal alkynes only Positive for all terminal alkynes only Positive for all alkynes
Amides	Basic (reflux) hydrolysis	All amides yield ammonia or the corresponding amine detected by odor or by placing wet blue litmus paper on top of the condenser
Amines	Diazotization Hinsberg test Solubility in dilute HCl	All 1° amines give red azodyes with $\beta$ -naphthol Distinguishes between 1°, 2°, and 3° All amines are soluble
Arenes	Aluminum chloride–chloroform	Positive for all arenes
Aryl halides	Aluminum chloride–chloroform	Positive for all aryl halides
Carboxylic acids	Solubility in dilute sodium bicarbonate Solubility in dilute sodium hydroxide	All carboxylic acids are soluble
Ketones	2,4-Dinitrophenylhydrazine (2,4-DNP) Hydrazine Iodoform Oxime Semicarbazone	Positive for all ketones (and aldehydes) Positive for all ketones (and aldehydes) Positive for methyl ketones Positive for all ketones (and aldehydes) Positive for all ketones (and aldehydes)
Nitriles	Basic hydrolysis	Positive for all nitriles
Phenols	Acetylation Benzoylation Sulfonation Ferric chloride test Solubility in aqueous base	ppt of a characteristic melting point ppt of a characteristic melting point ppt of a characteristic melting point Variety of colors characteristic of the individual phenol Most phenols are soluble in dilute sodium hydroxide but insoluble in dilute sodium bicarbonate; phenols with strong electron withdrawing groups (e.g., picric acid) are soluble in sodium bicarbonate
Sulfonamides	Basic (reflux) hydrolysis Sodium fusion test	Positive for all sulfonamides Presence of sulfur and nitrogen
Sulfonic acids	Sodium fusion test Solubility in aqueous base	Presence of sulfur Most sulfonic acids are soluble in dilute sodium hydroxide and generate carbon dioxide with sodium bicarbonate

*Note:* ppt = precipitate.

## INORGANIC GROUP QUALITATIVE TESTS

The following tables list some simple chemical tests that will indicate the presence or absence of a given inorganic cation or anion.<sup>1-4</sup> For most of these tests, the anion or cation must be present at a relatively high concentration; the approximate lower bound is 0.05% unless otherwise specified. It may therefore be necessary to concentrate more dilute samples before successful results can be obtained. Often, centrifuging solutions to clearly confirm the formation of a precipitate is necessary. These tests should be used in conjunction with other methods such as the chromatographic methods or spectrometry and spectrophotometry. Since many of these tests require the use of potentially toxic compounds, the strictest rules of laboratory safety must be observed at all times.\* The use of a fume hood is strongly recommended. All of the test reagents specified in this section are assumed to be in aqueous solution, unless otherwise designated. Refer to the work of Svehla and Suehla<sup>3</sup> for details on reagent preparation.

\*It is illegal to dispose of cyanide solutions in municipal sewer systems (POTW — publicly owned treatment works). The cyanide ion must be destroyed prior to disposal. This is easily done using an aqueous solution of chlorine:



The first step will occur at all pH levels; the second requires high pH; the third requires a pH near 7. Thus, careful acidification using HCl will complete the reaction, producing nitrogen and carbon dioxide.

## REFERENCES

1. Barber, H.H. and Taylor, T.I., *Semimicro Qualitative Analysis*, Harper Brothers, New York, 1953.
2. Bruno, T.J. and Svoronos, P.D.N., *Basic Tables for Chemical Analysis*, National Bureau of Standards Technical Note 1096, April 1986.
3. Svehla, G. and Suehla, G., *Vogel's Qualitative Inorganic Analysis*, 7th ed., Addison Wesley, New York, 1996.
4. De, A.K., *Separation of Heavy Metals*, Pergamon Press, New York, 1961.

## TESTS FOR ANIONS

This table provides a summary of the common tests for anions.

Tests for Anions	
<b>Acetates, <math>\text{CH}_3\text{COO}^-</math></b>	
Sulfuric acid, dilute	Evolution of acetic acid (vinegar-like odor); concentrated sulfuric acid also evolves sulfur dioxide under mild heating
Dry ethanol and concentrated sulfuric acid	Evolves ethyl acetate (fruity odor) upon heating; dry isoamyl alcohol may be substituted for ethanol
Silver nitrate	Formation of white precipitate of silver acetate that is soluble in dilute ammonia solution
Iron (III) chloride	Deep red coloration (coagulates on boiling forming a brownish red precipitate)
<b>Benzoates, <math>\text{C}_6\text{H}_5\text{COO}^-</math> (or <math>\text{C}_7\text{H}_5\text{O}_2^-</math>)</b>	
Dilute sulfuric acid	Formation of white precipitate of benzoic acid
Silver nitrate	White precipitate of silver benzoate from cold solutions; soluble in hot water and also in dilute ammonia solution
Iron (III) chloride	Buff-colored precipitate of iron (III) benzoate from neutral solution; soluble in hydrochloric acid
<b>Borates, <math>\text{BO}_3^{3-}</math>, <math>\text{B}_4\text{O}_7^{2-}</math>, <math>\text{BO}_2^-</math></b>	
Concentrated sulfuric acid	Upon heating solution, white fumes of boric acid are evolved
Silver nitrate	White precipitate of silver metaborate; soluble in dilute ammonia solution and in acetic acid
Barium chloride	White precipitate of barium metaborate that is soluble in excess reagent; dilutes acids as well as ammonium salt solutions
<b>Bromates, <math>\text{BrO}_3^-</math></b>	
Concentrated sulfuric acid	Evolution of red bromine vapors even in cold
Silver nitrate	White precipitate of silver bromate that is soluble in dilute ammonia
<i>Note:</i> Bromates are reduced to bromides by sulfur dioxide, hydrogen sulfide, or sodium nitrite solution	
<b>Bromides, <math>\text{Br}^-</math></b>	
Concentrated sulfuric acid	Reddish-brown coloration, followed by reddish-brown vapors (hydrogen bromide + bromine) evolution
Manganese dioxide + sulfuric acid	Reddish-brown bromine vapors evolve upon mild heating
Silver nitrate	Pale yellow, curdy, precipitate of silver bromide; slightly soluble in ammonia solution; insoluble in nitric acid
Lead acetate	White crystalline precipitate of lead bromide that is soluble in hot water
Special test: The addition of an aqueous solution of chlorine (or sodium hypochlorite) will liberate free bromine, which may be isolated in a layer of carbon tetrachloride or carbon disulfide	
<b>Carbonates, <math>\text{CO}_3^{2-}</math></b>	
Hydrochloric acid	Decomposition with effervescence and evolution of carbon dioxide (odorless)
Barium chloride	White precipitate of barium carbonate that is soluble in HCl (calcium chloride may be substituted for barium chloride)
Silver nitrate	Gray precipitate of silver carbonate
Special test: Effervescence with all acids, producing carbon dioxide, which makes limewater cloudy	
<b>Chlorates, <math>\text{ClO}_3^-</math></b>	
Concentrated sulfuric acid	Liberates chlorine dioxide gas (green); solids decrepitate (crackle explosively) when warmed; <i>large quantities may result in a violent explosion</i>

### Tests for Anions (continued)

Concentrated HCl	Chlorine dioxide gas evolved, imparts yellow color to acid
Manganese (II) sulfate + phosphoric acid	Violet coloration due to diphosphatomanganate formation; peroxydisulfate nitrates, bromates, iodates, and periodates react similarly
Heat of neat sample	Decomposition and formation of gaseous oxygen

#### Chlorides, $\text{Cl}^-$

Concentrated sulfuric acid	Evolution of hydrogen chloride gas (pungent odor)
Silver nitrate	White precipitate of silver chloride, which is soluble in ammonia solution (reprecipitate with $\text{HNO}_3$ )
Lead acetate	White precipitate of lead bromide; soluble in boiling water

Special test: 1.  $\text{MnO}_2 + \text{H}_2\text{SO}_4$  evolves  $\text{Cl}_2$  gas

2. An aqueous solution of chlorine + carbon disulfide produces no coloration

#### Chromates, $\text{CrO}_4^{2-}$ ; Dichromates, $\text{Cr}_2\text{O}_7^{2-}$

Barium chloride	Pale yellow precipitate of barium chromate; soluble in dilute mineral acids; insoluble in water and in acetic acid
Silver nitrate	Brownish red precipitate of silver chromate; soluble in dilute nitric acid and in ammonia solution; insoluble in acetic acid
Lead acetate	Yellow precipitate of lead chromate; soluble in dilute nitric acid; insoluble in acetic acid
Hydrogen peroxide	Deep blue coloration in acidic solution, which quickly turns green, with the liberation of oxygen
Hydrogen sulfide	Dirty yellow deposit of sulfur is produced in acidic solutions

#### Citrates, $\text{C}_6\text{H}_5\text{O}_7^{3-}$

Concentrated sulfuric	Evolution of carbon dioxide and carbon monoxide ( <i>caution: highly toxic</i> )
Silver nitrate	White precipitate of silver citrate that is soluble in dilute ammonia solution
Cadmium acetate	White gelatinous precipitate of cadmium citrate, practically insoluble in boiling water; soluble in warm acetic acid

#### Cyanates, $\text{OCN}^-$

Sulfuric acid, concentrated and dilute	Vigorous effervescence, due largely to evolution of carbon dioxide, with concentrated acid producing a more dramatic effect
Silver nitrate	Curdy white precipitate of silver cyanate
Copper sulfate–pyridine test	Lilac–blue precipitate (interference by thiocyanates); reagent is prepared by adding 2 or 3 drops of pyridine to 0.25 M $\text{CuSO}_4$ solution

#### Cyanides, $\text{CN}^-$

Cold dilute HCl	Liberation of hydrogen cyanide; odor of bitter almond ( <i>caution: highly toxic</i> )
Silver nitrate	White precipitate of silver cyanide
Concentrated sulfuric acid, hot	Liberation of carbon monoxide ( <i>caution: highly toxic</i> )
Mercury (I) nitrate	Gray precipitate of mercury
Copper sulfide	Formation of colorless tetracyanocuprate (I) ions; this test can be done on a section of filter paper

#### Dithionites, $\text{S}_2\text{O}_4^{2-}$

Dilute sulfuric acid	Orange coloration that disappears quickly, accompanied by evolution of sulfur dioxide gas and precipitation of pale yellow sulfur
Concentrated sulfuric acid	Fast evolution of sulfur dioxide and precipitation of pale yellow sulfur
Silver nitrate	Black precipitate of silver
Copper sulfate	Red precipitate of copper
Mercury (II) chloride	Gray precipitate of mercury
Methylene blue	Decolorization in cold solution
Potassium hexacyanoferrate (II) and iron (II) sulfate	White precipitate of dipotassium iron (II) hexacyanoferrate (II); turns from white to Prussian blue

## Tests for Anions (continued)

### Fluorides, F<sup>-</sup>

Concentrated sulfuric acid	Evolution of hydrogen fluoride dimer
Calcium chloride	White, slimy precipitate of calcium fluoride; slightly soluble in dilute hydrochloric acid
Iron (III) chloride	White precipitate

Special test: HF etches glass (only visible after drying)

### Formates, HCOO<sup>-</sup>

Dilute sulfuric acid	Formic acid is evolved (pungent odor)
Concentrated sulfuric acid	Carbon monoxide ( <i>highly poisonous</i> ) is evolved on warming
Ethanol and concentrated H <sub>2</sub> SO <sub>4</sub> , heat	Ethyl formate evolved (pleasant odor)
Silver nitrate	White precipitate of silver formate in neutral solutions, forming a black deposit of elemental silver upon mild heating
Iron (III) chloride	Red coloration due to complex formation
Mercury (II) chloride	White precipitate of calomel produced on warming; upon boiling, a black deposit of elemental mercury is produced

### Hexacyanoferrate (II) Ions, [Fe(CN)<sub>6</sub>]<sup>4-</sup>

Silver nitrate	White precipitate of silver hexacyanoferrate (II)
Iron (III) chloride	Prussian blue is formed in neutral or acid conditions, which is decomposed by alkali bases
Iron (II) sulfate (aq)	White precipitate of potassium iron (II) hexacyanoferrate, which turns blue by oxidation
Copper sulfate	Brown precipitate of copper hexacyanoferrate (II)
Thorium nitrate	White precipitate of thorium hexacyanoferrate (III)

### Hexacyanoferrate (III) Ions, [Fe(CN)<sub>6</sub>]<sup>3-</sup>

Silver nitrate	Orange-red precipitate of silver hexacyanoferrate (III), which is soluble in ammonia solution, but not in nitric acid
Iron (II) sulfate	Dark blue precipitate in neutral or acid solution (Prussian or Turnbull's blue)
Iron (III) chloride	Brown coloration
Copper sulfate	Green precipitate of copper (II) hexacyanoferrate (III)
Concentrated hydrochloric acid	In cold solution, brown precipitate of hexacyanoferric acid

### Hexafluorosilicates (Silicofluorides), [SiF<sub>6</sub>]<sup>2-</sup>

Barium chloride	White, crystalline precipitate of barium hexafluorosilicate; insoluble in dilute HCl; slightly soluble in water
Potassium chloride	White gelatinous precipitate of potassium hexafluorosilicate; slightly soluble in water
Ammonia solution	Gelatinous precipitate of silica acid

### Hydrogen Peroxide, H<sub>2</sub>O<sub>2</sub>

Potassium iodide and starch	If sample is previously acidified by dilute sulfuric acid, a deep blue coloration occurs attributed to the production of iodine complexation with starch
Potassium permanganate	Decolorization; evolution of oxygen
Titanium (IV) chloride	Orange-red coloration; very sensitive test

Special test:  $4\text{H}_2\text{O}_2 + \text{PbS} \rightarrow \text{PbSO}_4\downarrow + 4\text{H}_2\text{O}$

Black lead sulfide reacts to produce white lead sulfate

## Tests for Anions (continued)

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### Hypochlorites, $\text{OCl}^-$

Dilute hydrochloric acid	Yellow coloration, followed by chlorine gas evolution
Lead (II) acetate or nitrate	Brown lead (IV) oxide forms upon heating
Cobalt nitrate	Black precipitate of cobalt (II) hydroxide
Mercury	On shaking slightly acidified solution of a hypochlorite with Hg, a brown precipitate of mercury (II) chloride is formed

### Hypophosphites, $\text{H}_2\text{PO}_2^-$

Silver nitrate	White precipitate of silver hypophosphite
Mercury (II) chloride	White precipitate of calomel in cold solution, which darkens upon warming
Copper (II) sulfate	Upon warming red precipitate of copper (I) oxide forms
Potassium permanganate	Immediate decolorization under cold conditions

### Iodates, $\text{IO}_3^-$

Silver nitrate	White, curdy precipitate of silver iodate; soluble in dilute ammonia solution
Barium chloride	White precipitate of barium iodate; sparingly soluble in hot water or dilute nitric acid; insoluble in ethanol and methanol
Mercury (II) nitrate	White precipitate of mercury (II) iodate

### Iodides, $\text{I}^-$

Concentrated sulfuric acid	Produces hydrogen iodide and iodine
Silver (I) nitrate	Yellow ppt of silver (I) iodide, which is slightly soluble in ammonia solution and insoluble in dilute nitric acid
Lead acetate	Yellow precipitate of lead iodide; soluble in excess hot water
Potassium dichromate and concentrated sulfuric acid	Liberation of iodine
Sodium nitrite	Liberation of iodine
Copper sulfate	Brown mixed precipitate
Mercury (II) chloride	Scarlet precipitate of mercury (II) iodide

Special test: 1.  $\text{MnO}_2 + \text{H}_2\text{SO}_4$  produces  $\text{I}_2$   
2.  $\text{Cl}_2$  (aq)/ $\text{CS}_2$  produces  $\text{I}_2$  in  $\text{CS}_2$  (purple)  
3. Starch paste +  $\text{Cl}_2$  (aq), deep blue coloration

### Metaphosphates, $\text{PO}_3^-$

Silver nitrate	White precipitate; soluble in dilute nitric acid, dilute ammonia solution, and dilute acetic acid
Albumin and dilute acetic acid	Coagulation
Zinc sulfate solution	White precipitate on warming; soluble in dilute acetic acid

### Nitrates, $\text{NO}_3^-$

Concentrated sulfuric acid	Solid nitrate with concentrated sulfuric acid evolves reddish brown vapors of nitrogen dioxide + nitric acid vapors when heated
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Special test: 1. Add iron (II) sulfate, shake, and then add concentrated sulfuric acid; produces brown ring  
2. White precipitate is formed upon addition of nitron reagent ( $\text{C}_{20}\text{H}_{16}\text{N}_4$ ); test is not specific to only nitrates, however; see table of precipitation reagents

### Nitrites, $\text{NO}_2^-$

Dilute hydrochloric acid	Cautious addition of acid to a solid nitrite in cold gives a transient pale (of nitrous acid or the anhydride) blue liquid and evolves brown fumes of nitrogen dioxide
Silver nitrate	White precipitate of silver nitrite
Iron (II) sulfate solution (25%, acidified with either acetic or sulfuric acid)	A brown ring forms at the junction of the two liquids due to the formation of a complex



### Tests for Anions (continued)

Acidified potassium permanganate	Decolorization with no gas evolution
Ammonium chloride (solid)	Boiling with excess of solid reagent causes nitrogen to be evolved
Concentrated sulfuric acid	Liberates brown nitrogen dioxide gas

Special test: Acidified solutions of nitrites liberate iodine from potassium iodide

#### Orthophosphates, $\text{PO}_4^{3-}$

Silver nitrate	Yellow precipitate of silver orthophosphate; soluble in dilute ammonia and in dilute nitric acid
Barium chloride	White precipitate of barium hydrogen phosphate; soluble in dilute mineral acids and acetic acid
Magnesium nitrate reagent or magnesia mixture	White crystalline precipitate of magnesium ammonium phosphate; soluble in acetic acid and mineral acids; practically insoluble in 2.5% ammonia solution
Ammonium molybdate	Addition of 2 to 3 ml of excess reagent to approximately 0.5-ml sample gives yellow precipitate of ammonium phosphomolybdate, which is soluble in ammonia solution and in solutions of caustic alkalis; large quantities of hydrochloric acid interfere
Iron (III) chloride	Yellowish white precipitate of iron (III) phosphate; soluble in mineral acids; insoluble in dilute acidic acid
Ammonium molybdate–quinine	Yellow precipitate of unknown composition; reducing agents interfere

*Note:* The orthophosphates are salts of orthophosphoric acid,  $\text{H}_3\text{PO}_4$ , and are simply referred to as phosphates

#### Oxalates, $(\text{COO})_2^{2-}$

Silver nitrate	White precipitate of silver oxalate; soluble in ammonia solution and dilute nitric acid
Calcium chloride	White precipitate of calcium oxalate; insoluble in dilute acetic acid, oxalic acid, and ammonium oxalate solution; soluble in dilute hydrochloric acid and in dilute nitric acid
Potassium permanganate	Decolorization upon warming to 60 to 70°C, in acidified solution

#### Perchlorates, $\text{ClO}_4^-$

Potassium chloride	White precipitate of potassium perchlorate; insoluble in alcohol
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Special test: 1. Neutral  $\text{ClO}_4^-$  + cadmium sulfate in concentrated ammonia produces  $[\text{Cd}(\text{NH}_3)_4](\text{ClO}_4)_2$  (white precipitate)  
2. Cautious heating of solids evolves oxygen

#### Peroxydisulfates, $\text{S}_2\text{O}_8^{2-}$

Water	On boiling, decomposes into the sulfate, free sulfuric acid, and oxygen
Silver nitrate	Black precipitate of silver peroxide
Barium chloride	On boiling or standing for some time, forms precipitate of barium sulfate
Manganese (II) sulfate	Brown precipitate of hydrate complex in neutral or alkaline test solution

#### Phosphites, $\text{HPO}_3^{2-}$

Silver nitrate	White precipitate of silver phosphite, which yields black metallic silver on standing
Barium chloride	White precipitate of barium phosphite; soluble in dilute acids
Mercury(II) chloride	White precipitate in cold solutions, which yields gray metallic mercury on warming
Copper sulfate	Light blue precipitate that dissolves in hot acetic acid
Lead (II) acetate	White precipitate of lead (II) hydrogen phosphite

#### Pyrophosphates, $\text{P}_2\text{O}_7^{4-}$

Silver nitrate	White precipitate; soluble in dilute nitric acid and in dilute acetic acid
Copper sulfate	Pale blue precipitate

### Tests for Anions (continued)

Magnesia mixture or magnesium reagent	White precipitate; soluble in excess reagent but reprecipitated on boiling
Cadmium acetate and dilute acetic acid	White precipitate
Zinc sulfate	White precipitate; insoluble in dilute acetic acid; soluble in dilute ammonia solution, yielding a white precipitate on boiling

#### Salicylates, $\text{C}_6\text{H}_4(\text{OH})\text{COO}^-$ (or $\text{C}_7\text{H}_5\text{O}_3^-$ )

Concentrated sulfuric acid	Evolution of carbon monoxide and sulfur dioxide (poisonous)
Concentrated sulfuric acid and methanol	0.5 g of sample + 3 ml of reagent + heat evolves methyl salicylate (odor of wintergreen)
Dilute hydrochloric acid	Crystalline precipitate of salicylic acid
Silver nitrate	Heavy crystalline precipitate of silver salicylate (which is soluble in boiling water and recrystallizes upon cooling)
Iron (III) chloride	Violet–red coloration that clears upon the addition of dilute mineral acids

#### Silicates, $\text{SiO}_3^{2-}$

Dilute hydrochloric acid	Gelatinous precipitate of metasilicic acid; insoluble in concentrated acids; soluble in water and dilute acids
Ammonium chloride or ammonium carbonate	Gelatinous precipitate
Silver nitrate	Yellow precipitate of silver silicate; soluble in dilute acids as well as ammonia solution
Barium chloride	White precipitate of barium silicate that is soluble in dilute nitric acid

#### Succinates, $\text{C}_4\text{H}_4\text{O}_4^{2-}$

Silver nitrate	White precipitate of silver succinate; soluble in dilute ammonia solution
Iron (III) chloride	Light brown precipitate of iron (III) succinate
Barium chloride	White precipitate of barium succinate
Calcium chloride	Precipitate of calcium succinate appears slowly

#### Sulfates, $\text{SO}_4^{2-}$

Barium chloride	White precipitate of barium sulfate; insoluble in warm dilute hydrochloric acid and in dilute nitric acid; slightly soluble in boiling hydrochloric acid
Lead acetate	White precipitate of lead sulfate; soluble in hot concentrated sulfuric acid, ammonium acetate, ammonium tartrate, and sodium hydroxide
Silver nitrate	White precipitate of silver sulfate
Mercury (II) nitrate	Yellow precipitate of mercury (II) sulfate

#### Sulfides, $\text{S}^{2-}$

Dilute hydrochloric acid or sulfuric acid	Hydrogen sulfide gas is evolved and detected by odor or lead acetate paper
Silver nitrate	Black precipitate of silver sulfide; soluble in hot, dilute nitric acid
Lead acetate	Black precipitate of lead sulfide
Sodium nitroprusside solution ( $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$ )	Transient purple color in the presence of solutions of alkalis
Special test: Catalysis of iodine–azide reaction: solution of sodium azide ( $\text{NaN}_3$ ) and iodine reacts with a trace of a sulfide to evolve nitrogen; thiosulfates and thiocyanates act similarly and therefore must be absent	

#### Sulfites, $\text{SO}_3^{2-}$

Dilute hydrochloric acid	Decomposition (which becomes more rapid on warming) and evolution of sulfur dioxide (odor of burning sulfur)
Barium chloride Strontium chloride	White precipitate of the respective sulfite, the precipitate being soluble in dilute hydrochloric acid
Silver nitrate	At first no change; upon addition of more reagent, white crystalline precipitate at silver sulfite forms, which darkens to metallic silver upon heating

### Tests for Anions (continued)

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Potassium permanganate solution acidified with dilute sulfuric acid	Decolorization (Fuchsin test)
Potassium dichromate in with dilute sulfuric acid	Green color formation
Lead acetate or lead nitrate solution	White precipitate of lead sulfite
Zinc and sulfuric acid	Hydrogen sulfide gas evolved, detected by holding lead acetate paper to mouth of test tube
Concentrated sulfuric acid	Evolution of sulfur dioxide gas
Sodium nitroprusside–zinc sulfate	Red compound of unknown composition

#### Tartrates, $\text{C}_4\text{H}_4\text{O}_6^{2-}$

Concentrated sulfuric acid	When sample is heated, the evolution of carbon monoxide, carbon dioxide, and sulfur dioxide (burnt sugar odor) results
Silver nitrate	White precipitate of silver tartrate
Calcium chloride	White precipitate of calcium tartrate; soluble in dilute acetic acid, dilute mineral acids, and in cold alkali solutions
Potassium chloride	White precipitate, the reaction is: $\text{C}_4\text{H}_4\text{O}_6^{2-} + \text{K}^+ + \text{CH}_3\text{COOH} \rightarrow \text{C}_4\text{H}_5\text{O}_6 \text{K} \downarrow + \text{CH}_3\text{COO}^-$
Special test: One drop of 25% iron (II) sulfate, 2 or 3 drops of hydrogen peroxide: produces deep violet–blue color (Fenton's test)	

#### Thiocyanates, $\text{SCN}^-$

Sulfuric acid	In cold solution, yellow coloration is produced; upon warming, violent reaction occurs and carbonyl sulfide is formed
Silver nitrate	White precipitate of silver thiocyanate
Copper sulfate	First a green coloration, then black precipitate of copper (II) thiocyanate is formed
Mercury (II) nitrate	White precipitate of mercury (II) thiocyanate
Iron (III) chloride	Blood red coloration due to complex formation
Dilute nitric acid	Upon warming, red coloration is observed, with nitrogen oxide and hydrogen cyanide ( <i>caution: toxic</i> ) being evolved
Cobalt nitrate	Blue coloration due to complex ion formation

#### Thiosulfates, $\text{S}_2\text{O}_3^{2-}$

Iodine solution	Decolorized; a colorless solution of tetrathionate ions is formed
Barium chloride	White precipitate of barium thiosulfate
Silver nitrate	White precipitate of silver thiosulfate
Lead (II) acetate or nitrate solution	First no change; on further addition of reagent, a white precipitate of lead thiosulfate forms
Iron (III) chloride solution	Dark violet coloration due to complex formation
Nickel ethylenediamine nitrate $[\text{Ni}(\text{NH}_2(\text{CH}_2)_2\text{NH}_2)_3](\text{NO}_3)_2$	Violet complex precipitate forms; hydrogen sulfide and ammonium sulfide interfere
Special test: Blue ring test — when solution of thiosulfate mixed with ammonium molybdate solution is poured slowly down the side of a test tube that contains concentrated sulfuric acid, a blue ring is formed temporarily at the contact zone	

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## TESTS FOR CATIONS

This table provides a summary of the common tests for cations, primarily in aqueous solution. The cations are grouped according to the usual convention of reactivity to a set of common reagents.

Abbreviations in the table are as follows:

conc	concentrated
dil	dilute
g	gaseous
EtOH	ethanol

### Tests for Cations

#### Group I: Pb, Ag, Hg(I)

All members are precipitated by dilute HCl, to give lead chloride ( $\text{PbCl}_2$ ), silver chloride ( $\text{AgCl}$ ), or mercury (I) chloride ( $\text{Hg}_2\text{Cl}_2$ ).

Lead (II),  $\text{Pb}^{+2}$

Potassium chromate	Yellow precipitate of lead (II) chromate
Potassium iodide	Yellow precipitate of lead (II) iodide
Sulfuric acid, dilute	White precipitate of lead (II) sulfate
Hydrogen sulfide gas	Black precipitate of lead (II) sulfide
Potassium cyanide	White precipitate of lead (II) cyanide
Tetramethyldiaminodiphenyl-methane	Blue oxidation product (presence of Bi, Ce, Mn, Th, Co, Ni, Fe, Cu may interfere)
Gallocyanine	Deep violet precipitate; unknown composition (Bi, Cd, Cu, Ag interfere)
Diphenylthiocarbazone	Brick red complex in neutral or ammoniacal solution

Silver (I),  $\text{Ag}^+$

Potassium chromate	Reddish brown precipitate of silver chromate
Potassium iodide	Yellow precipitate of silver iodide
Hydrogen sulfide gas	Black precipitate of silver sulfide
Disodium hydrogen phosphate	Yellow precipitate of silver phosphate
Sodium carbonate	Yellow-white precipitate of silver carbonate, forming a brown oxide upon heating
<i>p</i> -Dimethylaminobenzylidene-rhodanine	Reddish violet precipitate in acidic solution
Ammonia solution	Brown precipitate of silver oxide, dissolving in excess to form $\text{Ag}_3\text{N}$ , which is explosive

Mercury (I),  $\text{Hg}_2^{+2}$

Potassium carbonate	Red precipitate of mercury (I) chromate
Potassium iodide	Green precipitate of mercury (I) iodide
Dilute sulfuric acid	White precipitate of mercury (I) sulfate
Elemental copper, aluminum, or zinc	Amalgamation occurs
Hydrogen sulfide	Black precipitate (in neutral or acid medium) of mercury (I) sulfide and mercury
Ammonia solution	Black precipitate of $\text{HgO} \cdot \text{Hg}(\text{NH}_2)(\text{NO}_3)$
Diphenylcarbazide (1% in ethanol, with 0.2 M nitric acid)	Violet colored complex results (high sensitivity and selectivity)
Potassium cyanide	Mercury (I) cyanide solution, with a precipitation of elemental mercury (mercury (II) interferes)

#### Group II: Hg(II), Cu, Bi, Cd, As(III), As(V), Sb(III), Sb(V), Sn(II), Sn(IV)

All members show no reaction with HCl; all form a precipitate with  $\text{H}_2\text{S}$ .

Bismuth (III),  $\text{Bi}^{3+}$

Potassium iodide	Black precipitate of bismuth (III) iodide
Potassium chromate	Yellow precipitate of bismuth (III) chromate
Ammonia solution	White precipitate of variable composition; approximate formula: $\text{Bi}(\text{OH})_2\text{NO}_3$

### Tests for Cations (continued)

Pyrogallol (10%)	Yellow precipitate of bismuth (III) pyrogallate
8-Hydroxyquinoline (5%) + potassium iodide (6 M)	Red precipitate of the tetraiodobismuthate salt (characteristic in the absence of $\text{Cl}^-$ , $\text{F}^-$ , $\text{Br}^-$ )
Sodium hydroxide	White precipitate of bismuth (III) hydroxide
Copper (II), $\text{Cu}^{+2}$	
Potassium iodide	Brown precipitate of copper (I) iodide, colored brown due to $\text{I}_3^-$
Potassium cyanide	Yellow precipitate of copper (II) cyanide, which then decomposes
Potassium thiocyanate	Black precipitate of copper (II) thiocyanate, which then decomposes
$\alpha$ -Benzoin oxime (or cupfon), 5% in EtOH	Green precipitate of the $\alpha$ -benzoin oxime salt derivative
Salicylaldoxime (1%)	Greenish yellow precipitate of the copper complex
Rubeanic acid (0.5%) (dithio-oxamide)	Black precipitate of the rubeanate salt
Cadmium (II), $\text{Cd}^{2+}$	
Ammonia solution	White precipitate of cadmium hydroxide, which dissolves in excess ammonia
Potassium cyanide	White precipitate of cadmium cyanide, which dissolves in excess potassium cyanide
Sodium hydroxide	White precipitate of cadmium hydroxide, which is insoluble in excess sodium hydroxide
Dinitro- <i>p</i> -diphenyl carbazide	Brown precipitate with cadmium hydroxide
Arsenic (III), $\text{As}^{+3}$	
Silver nitrate	Yellow precipitate of silver arsenite in neutral solution
Copper (II) sulfate	Green precipitate of copper (II) arsenite (or $\text{Cu}_3(\text{AsO}_3)_2 \cdot x\text{H}_2\text{O}$ )
Potassium tri-iodide ( $\text{KI} + \text{I}_2$ )	Becomes decolorized upon oxidation
Tin (II) chloride + concentrated hydrochloric acid	Black precipitate forms in the presence of excess reagent
Arsenic (V), $\text{As}^{+5}$	
Silver nitrate	Brownish red precipitate of silver arsenate from neutral solutions
Ammonium molybdate	Yellow precipitate (in presence of excess reagent) of ammonium arsenomolybdate $(\text{NH}_4)_3\text{AsMo}_{12}\text{O}_{40}$
Potassium iodide + concentrated hydrochloric acid	Iodine formation
<i>Note:</i> Small amounts of As(III) or As(V) can be identified by the response to the Marsh, Gutzeit, or Fleitmann tests (see references at the beginning of this section)	
Antimony (III), $\text{Sb}^{+3}$	
Sodium hydroxide	White precipitate of the hydrated oxide $\text{Sb}_2\text{O}_3 \cdot x\text{H}_2\text{O}$
Elemental zinc or tin	Black precipitate of antimony
Potassium iodide	Yellow color of $[\text{SbI}_6]^{3-}$ ion
Phosphomolybdic acid, $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$	Blue color produced; Sn(II) interferes; sensitivity, 0.2 $\mu\text{g}$
Antimony (V), $\text{Sb}^{+5}$	
Water	White precipitate of basic salts, and ultimately antimonous acid, $\text{H}_3\text{SbO}_4$
Potassium iodide	Formation of iodine as a floating precipitate
Elemental zinc or tin	Black precipitate of antimony (in the presence of hydrochloric acid)
<i>Note:</i> Small amounts of antimony can be identified using the Marsh or Gutzeit test (see references at the beginning of this section for details)	
Tin (II), $\text{Sn}^{+2}$	
Mercury (II) chloride	White precipitate of mercury (I) chloride (in an excess of tin ions, precipitate turns gray)
Bismuth nitrate	Black precipitate of bismuth metal
Cacotheline (nitro-derivative of brucine, $\text{C}_{21}\text{H}_{21}\text{O}_7\text{N}_3$ )	Violet coloration with stannous salts; the following interfere: strong reducing agents (hydrogen sulfide, dithionites, sulfites, and selenites); also, U, V, Te, Hg, Bi, Au, Pd, Se, Sb

### Tests for Cations (continued)

Diazine green (dyestuff formed by coupling diazotized safranine with <i>N,N</i> -dimethylaniline)	Color change: blue → violet → red
Tin (IV), $\text{Sn}^{+4}$ Iron powder	Reduces $\text{Sn(IV)}$ to $\text{Sn(II)}$
<b>Group III: Fe (II) and (III), <math>\text{Al}^{3+}</math>, Cr (III) and (VI), <math>\text{Ni}^{2+}</math>, <math>\text{Co}^{2+}</math>, Mn (II) and (VII), and <math>\text{Zn}^{2+}</math></b>	
All members are precipitated by $\text{H}_2\text{S}$ in the presence of ammonia and ammonium chloride, or ammonium sulfide solutions.	
Iron (II), $\text{Fe}^{+2}$	
Ammonia solution	Precipitation of iron (II) hydroxide; if large amounts of ammonium ion are present, precipitation does not occur
Ammonium sulfide	Black precipitate of iron (II) sulfide
Potassium cyanide ( <i>poison</i> )	Yellowish brown precipitate of iron (II) cyanide; soluble in excess reagent, forming the hexacyanoferrate (II) ion
Potassium hexacyanoferrate (II) solution	In complete absence of air, white precipitate of potassium iron (II) hexacyanoferrate; if air is present, a pale blue precipitate is formed
Potassium hexacyanoferrate (III) solution $\alpha, \alpha'$ -Dipyridyl	Dark blue precipitate, called Turnbull's blue Deep red bivalent cation $[\text{Fe}(\text{C}_5\text{H}_4\text{N})_2]^{2+}$ formed with iron (II) salts in mineral acid solution; sensitivity, 0.3 $\mu\text{g}$
Dimethylglyoxime (DMG)	Red, iron (II) dimethylglyoxime; nickel, cobalt, and large quantities of copper salts interfere; sensitivity, 0.04 $\mu\text{g}$
<i>o</i> -Phenanthroline (0.1 wt% in water)	Red coloration due to the complex cation $[\text{Fe}(\text{C}_{12}\text{H}_8\text{N}_2)_3]^{2+}$ , in slightly acidic conditions
Iron (III), $\text{Fe}^{+3}$	
Ammonia solution	Reddish brown gelatinous precipitate of iron (III) hydroxide
Ammonium sulfide	Black precipitate mixture of iron (II) sulfide and sulfur
Potassium cyanide	When added slowly, reddish brown precipitate of iron (III) cyanide is formed, which dissolves in excess potassium cyanide to yield a yellow solution
Potassium hexacyanoferrate (III)	A brown coloration is produced due to formation of iron (III) hexacyanoferrate (III)
Disodium hydrogen phosphate	Yellowish white precipitate of iron (III) phosphate
Sodium acetate solution	Reddish brown coloration caused by complex formation
Cupferron ( $\text{C}_6\text{H}_5\text{N}(\text{NO})\text{ONH}_4$ ) aqueous solution, freshly prepared	Reddish brown precipitate formed in the presence of hydrochloric acid
Ammonium thiocyanate + dilute acid	Deep red coloration of iron (III) thiocyanate complex
7-Iodo-8-hydroxyquinoline-5-sulfonic acid (ferron)	Green or greenish blue coloration in slightly acidic solutions; sensitivity, 0.5 $\mu\text{g}$
Cobalt (II), $\text{Co}^{+2}$	
Ammonia solution	In the absence of ammonium salts, small amounts of $\text{Co(OH)NO}_3$ precipitate, which is soluble in excess
Ammonium sulfide	Black precipitate of cobalt (II) sulfide, from neutral or alkaline solutions
Potassium cyanide ( <i>poison</i> )	Reddish brown precipitate of cobalt (II) cyanide, which dissolves in excess
Potassium nitrite	Yellow precipitate of potassium hexacyanocobaltate (III), $\text{K}_3[\text{Co}(\text{NO}_2)_6]$
Ammonium thiocyanate (crystals)	Gives blue coloration when added to neutral or acid solution of cobalt, due to a complex formation (Vogel's reaction); sensitivity, 0.5 $\mu\text{g}$
$\alpha$ -Nitroso- $\beta$ -naphthol (1% in 50% acetic acid)	Red-brown (chelate) precipitate, extractable using carbon tetrachloride; sensitivity, 0.05 $\mu\text{g}$
Nickel (II), $\text{Ni}^{+2}$	
Ammonia solution	Green precipitate of nickel (II) hydroxide, which dissolves in excess ammonia
Potassium cyanide ( <i>poison</i> )	Green precipitate of nickel (II) cyanide, which dissolves in excess potassium cyanide
Dimethylglyoxime ( $\text{C}_4\text{H}_8\text{O}_2\text{N}_2$ )	Red precipitate of nickel–DMG chelate complex in ammoniacal solution; sensitivity, 0.16 $\mu\text{g}$

### Tests for Cations (continued)

Manganese (II), $Mn^{+2}$	
Ammonia solution	Partial precipitation of white manganese (II) hydroxide
Ammonium sulfide	Pink precipitate of manganese (II) sulfide, which is soluble in mineral acids
Sodium phosphate (in the presence of ammonia or ammonium ions)	Pink precipitate of manganese ammonium phosphate, $Mn(NH_4)PO_4 \cdot 7H_2O$ , which is soluble in acids
Aluminum (III), $Al^{3+}$	
Ammonia	White gelatinous precipitate of aluminum hydroxide
Sodium hydroxide	White precipitate of aluminum hydroxide; soluble in excess sodium hydroxide
Ammonium sulfide	White precipitate of aluminum sulfide
Sodium acetate	Upon boiling with excess reagent, a precipitate of basic aluminum acetate, $Al(OH)_2CH_3COO$ , is formed
Sodium phosphate	White gelatinous precipitate of aluminum phosphate
Aluminon (a solution of the ammonium salt of aurine tricarboxylic acid)	Bright red solution
Quinalizarin, alizarin-S, alizarin	Red precipitate or "lake"
Chromium (III), $Cr^{+3}$	
Ammonia solution	Gray-green to gray-blue gelatinous precipitate of chromium (III) hydroxide
Sodium carbonate	Precipitate of chromium (III) hydroxide
Zinc (II), $Zn^{2+}$	
Ammonia solution	White precipitate of zinc hydroxide; soluble in excess ammonia
Disodium hydrogen phosphate	White precipitate of zinc phosphate; soluble in dilute acids
Potassium hexacyanoferrate (II)	White precipitate of variable composition, which is soluble in sodium hydroxide
Ammonium tetrathiocyanato-mercurate (II)-copper sulfate, slightly acidic	Solution is treated with 5 drops of 0.25 M copper (II) sulfate solution followed by 2 ml of ammonium tetrathiocyanato-mercurate to give a violet precipitate

### Group IV: $Ba^{2+}$ , $Sr^{2+}$ , $Ca^{2+}$

All members of this group react with ammonium carbonate.

Barium (II), $Ba^{+2}$	
Ammonium carbonate	White precipitate of barium carbonate; soluble in dilute acids
Ammonium oxalate	White precipitate of barium oxalate; soluble in dilute acids
Dilute sulfuric acid	Heavy, white, finely divided precipitate of barium sulfate
Saturated calcium sulfate (or strontium sulfate)	White precipitate of barium sulfate
Sodium rhodizonate	Red-brown precipitate; sensitivity, 0.25 $\mu g$
Strontium (II), $Sr^{+2}$	
Ammonium carbonate	White precipitate of strontium carbonate
Dilute sulfuric acid	White precipitate of strontium sulfate
Saturated calcium sulfate	White precipitate of strontium sulfate
Potassium chromate	Yellow precipitate of strontium chromate
Ammonium oxalate	White precipitate of strontium oxalate, which is soluble in mineral acids
Calcium (II), $Ca^{+2}$	
Ammonium carbonate	White precipitate of calcium carbonate
Dilute sulfuric acid	White precipitate of calcium sulfate
Ammonium oxalate	White precipitate of calcium oxalate, which is soluble in mineral acids
Potassium chromate	Yellow precipitate of strontium chromate, which is soluble in mineral acids
Sodium rhodizonate	Red-brown precipitate; sensitivity, 4 $\mu g$

### Group V: $Mg$ , $Na$ , $K$ , $NH_4^+$

No common reaction or reagent.

Magnesium (II), $Mg^{2+}$	
Ammonia solution, sodium hydroxide	Partial precipitation of white magnesium hydroxide
Ammonium carbonate	White precipitate of magnesium carbonate, only in the absence of ammonia salts

### Tests for Cations (continued)

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Oxine + ammoniacal ammonium chloride solution	Yellow precipitate of $\text{Mg}(\text{C}_9\text{H}_6\text{NO})_2 \cdot 4\text{H}_2\text{O}$
Quinalizarin	Blue precipitate or blue-colored solution, which can be cleared by a few drops of bromine–water
Sodium (I), $\text{Na}^+$	
Uranyl magnesium acetate solution (in 30 v/v ETOH)	Yellow precipitate of sodium magnesium uranyl acetate
Uranyl zinc acetate solution	Yellow precipitate of sodium zinc uranyl acetate; sensitivity, 12.5 $\mu\text{g}$ of Na
Potassium (I), $\text{K}^+$	
Sodium hexanitrocobaltate (III) ( $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$ )	Yellow precipitate of potassium hexanitrocobaltate (III); insoluble in acetic acid
Tartaric acid solution (sodium acetate buffered)	White precipitate of potassium hydrogen tartrate
Perchloric acid	White precipitate of potassium perchlorate
Dipicrylamine	Orange-red complex precipitate ( $\text{NH}_4^+$ interferes); sensitivity, 3 $\mu\text{g}$ of K
Sodium tetraphenylboron + acetic acid	White precipitate of the potassium salt
Ammonium, $\text{NH}_4^+$	
Sodium hydroxide	Evolution of ammonia gas upon heating
Potassium tetraiodomercurate (Nessler's reagent)	Brown-yellow color or brown precipitate of mercury (II) amidoiodide; high sensitivity; all other metals (except Na and K) interfere
Tannic acid–silver nitrate	Precipitate of black elemental silver, from neutral solution; very sensitive
<i>p</i> -Nitrobenzene–diazonium chloride	Red-colored solution results in the presence of sodium hydroxide; sensitivity, 0.7 $\mu\text{g}$ of $\text{NH}_4^+$

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*Note:* Ammonium ions will cause a similar reaction to that of potassium in the presence of: sodium hexanitrocobaltate (III) sodium hydrogen tartrate.

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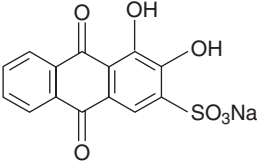
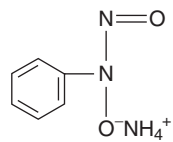
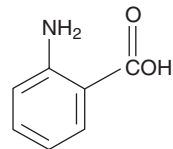
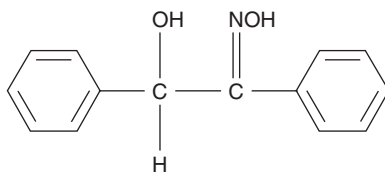
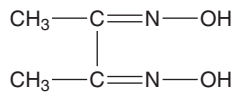
## ORGANIC PRECIPITATION REAGENTS FOR INORGANIC IONS

The following table lists the most important organic reagents used for precipitating various inorganic species from solution.<sup>1,2</sup> Many of these reagents are subject to the serious disadvantages caused by lack of selectivity. Thus, many of the listed reagents will precipitate more than one species. The selectivity of some of the reagents can be controlled to a certain extent by adjustment of pH, reagent concentrations, and the use of masking reagents. The first two factors, pH and concentration, are the most critical. A number of these reagents form rather large, bulky complexes. While this can serve to enhance sensitivity (especially for gravimetric procedures), it can also impose rather stringent concentration limits. Refer to several excellent recipe texts for further guidance.<sup>3-10</sup>

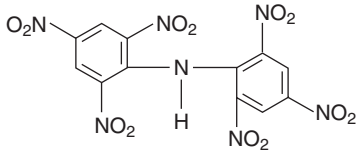
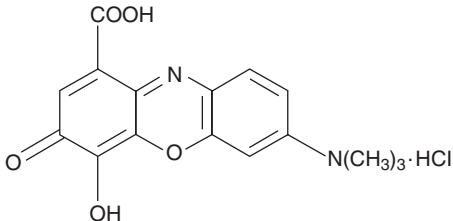
## REFERENCES

1. Kennedy, J.H., *Analytical Chemistry*, 2nd ed., Saunders College Publishing, New York, 1990.
2. Christian, G.D., *Analytical Chemistry*, 5th ed., John Wiley & Sons, New York, 1994.
3. Barber, H.H. and Taylor, T.I., *Semimicro Qualitative Analysis*, Harper and Brothers, New York, 1953.
4. Greenfield, S. and Clift, M., *Analytical Chemistry of the Condensed Phosphates*, Pergamon Press, Oxford, 1975.
5. Ryabchikov, D.I. and Gol'Braikh, E.K., *The Analytical Chemistry of Thorium*, Macmillan Company, New York, 1963.
6. Jungreis, E., *Spot Test Analysis*, Wiley Interscience, New York, 1985.
7. Jungreis, E., *Spot Test Analysis: Clinical, Environmental, Forensic and Geochemical Applications*, 2nd ed., John Wiley & Sons, New York, 1997.
8. Svehla, G. and Suehla, G., *Vogel's Qualitative Inorganic Analysis*, Addison-Wesley, New York, 1996.
9. Skoog, D.A., West, D.M., and Holler, F.J., *Fundamentals of Analytical Chemistry*, 7th ed., Saunders College Publishing, New York, 1996.
10. Harris, D.C., *Quantitative Chemical Analysis*, 5th ed., Freeman, New York, 1997.

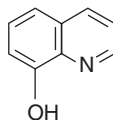
## Organic Precipitation Reagents

Reagent	Structure/Formula	Applications and Notes
Alizarin-S (sodium alizarin sulfonate)		Will precipitate Al in ammoniacal solution; high sensitivity
Ammonium nitrosophenylhydroxylamine (cupferron)		Will precipitate Fe(III), V(V), Ti(IV), Zr(IV), Sn(IV), U(IV) in the presence of moderate acidity; will also precipitate rare earths
Anthranilic acid		Will precipitate Cu(II), Cd(II), Ni(II), Co (II), Pb(II), Zn(II) in acetic acid or nearly neutral solution
$\alpha$ -Benzoin oxime (cupron)		Will precipitate Cu(II) in the presence of NH <sub>3</sub> or tartarate; will precipitate Mo(VI), W(VI) in acidic medium
Dimethylglyoxime (DMG)		Will precipitate Ni(II) in the presence of NH <sub>3</sub> or buffered acetate; Pd(II) in HCl solution; the addition of tartaric acid to the reagent will mask Fe(III) and Cr(III) interferences; Pd(II) and Bi(III) will also precipitate

### Organic Precipitation Reagents (continued)

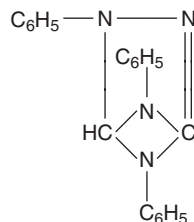
Reagent	Structure/Formula	Applications and Notes
Dimethyl oxalate	$\text{H}_3\text{C}-\text{O}-\overset{\overset{\text{O}}{\parallel}}{\text{C}}-\overset{\overset{\text{O}}{\parallel}}{\text{C}}-\text{O}-\text{CH}_3$	Will precipitate Ac, Am, Ca, Th ions as well as rare earth metals
Dimethyl sulfate	$\text{CH}_3\text{O}-\overset{\overset{\text{O}}{\parallel}}{\underset{\underset{\text{O}}{\parallel}}{\text{S}}}-\text{OCH}_3$	Will precipitate Ba, Ca, Pb(II), Sr ions; particular care must be taken while using this reagent since it is a powerful methylating agent
Dipicrylamine (hexanitrodiphenylamine)		Will precipitate K <sup>+</sup> (as well as NH <sub>4</sub> , Na, and Li ions, but with much less sensitivity)
Dithiooxamide (rubeanic acid)	$\text{H}_2\text{N}-\overset{\overset{\text{S}}{\parallel}}{\text{C}}-\overset{\overset{\text{S}}{\parallel}}{\text{C}}-\text{NH}_2$	Will precipitate Cu(II) (black), Ni (blue), and Co (brown); high sensitivity
Gallocyanine		Will precipitate lead (deep violet precipitate of uncertain composition); high sensitivity

8-Hydroxyquinoline (oxine)



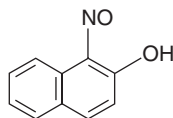
Will precipitate Al(III) at pH 4–5, and Mg(II) in the presence of  $\text{NH}_3$ ; will precipitate Be, Bi, Cd, Cu, Ga(I), Hf, Fe, In, Mg, Hg(II), Nb, Pd, Sc, Ta, Ti, Th, U, Zn, Zr, W ions at pH 4–5 or in the presence of  $\text{NH}_3$ ; use of pH control provides a measure of selectivity

Nitron reagent (in acetic acid)



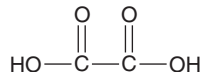
Will precipitate nitrate, bromide, iodide, nitrite, chromate chlorate, perchlorate, thiocyanate, oxalate, and picrate anions

$\alpha$ -Nitroso- $\beta$ -naphthol



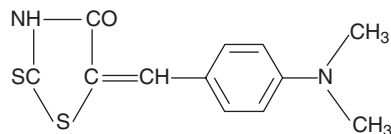
Will precipitate Co(II),  $\text{Ni}^{2+}$ , Fe(III), and Pd(II) in a weakly acidic solution

Oxalic acid



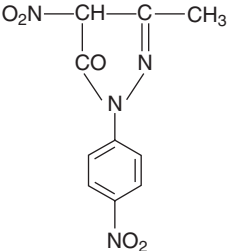
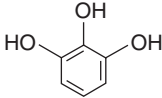
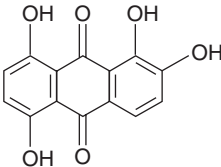
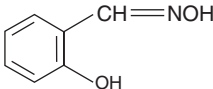
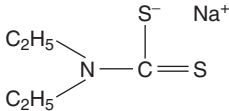
Will precipitate  $\text{Ca}^{+2}$ ; high concentrations of Mg will interfere

*p*-Dimethylamino-benzylidenerhodanine  
(0.3% in acetone)

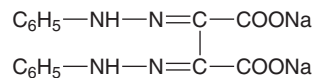


Will precipitate Ag(I), Hg(II), Au(II), Pt(II), Pd(II) under slightly acidic conditions

### Organic Precipitation Reagents (continued)

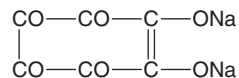
Reagent	Structure/Formula	Applications and Notes
Picrolonic acid		Will precipitate $\text{Ca}^{+2}$ ; subject to interference from many other cations, however
Pyrogallol		Will precipitate $\text{Bi(III)}$ and $\text{Sb(III)}$ ; high sensitivity
Quinalizarin		Will precipitate $\text{Al}^{+3}$
Salicylaldoxime (1% in acetic acid)		Will precipitate $\text{Cu(II)}$ , with interference by $\text{Pd(II)}$ and $\text{Au(II)}$
Sodium diethylthiocarbamate		Useful for the precipitation of many metals

Sodium dihydroxytartrate osazone



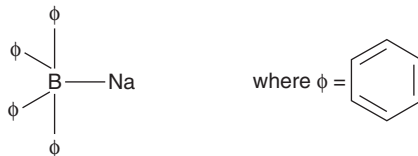
Will precipitate  $\text{Ca}^{+2}$ ; subject to interference from many other cations, however

Sodium rhodizionate



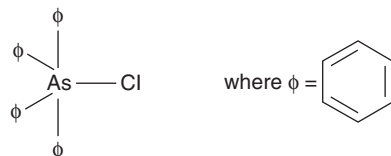
Will precipitate  $\text{Ba}^{+2}$  and  $\text{Sr}^{+2}$ ; subject to interference by all  $\text{H}_2\text{S}$  reactive cations

Sodium tetraphenylboron



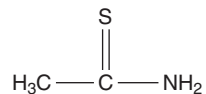
Used to precipitate K, Rb, Cs, Tl, Ag,  $\text{Hg(I)}$ ,  $\text{Cu(I)}$ ,  $\text{NH}_4^+$ ,  $\text{RNH}_3^+$ ,  $\text{R}_2\text{NH}_2^+$ ,  $\text{R}_3\text{NH}^+$ ,  $\text{R}_4\text{N}^+$ , in cold acidic solution; selectivity is high for  $\text{K}^+$  and  $\text{NH}_4^+$

Tetraphenyl arsonium chloride



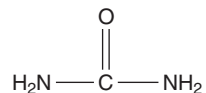
Will precipitate  $\text{Cr}_2\text{O}_7^{2-}$ ,  $\text{MnO}_4^-$ ,  $\text{ReO}_4^-$ ,  $\text{MoO}_4^{2-}$ ,  $\text{WO}_4^{2-}$ ,  $\text{ClO}_4^-$ ,  $\text{I}_3^-$  in acidic solution

Thioacetamide



Used to provide a source of  $\text{H}_2\text{S}$  for the precipitation of As, Bi, Cd, Cu, Hg, Mn, Mo, Pb, Sb, Sn with heating in acid medium

Urea



Will precipitate Al,  $\text{Fe(III)}$ , Ga, Sn, Th, Zn ions

**Organic Precipitation Reagents (continued)**

Reagent	Structure/Formula	Applications and Notes
Triethyl phosphate	$(C_2H_5O)_3PO$ $  \begin{array}{c}  O \\     \\  H_5C_2O - P - OC_2H_5 \\    \\  OC_2H_5  \end{array}  $	Will precipitate Hf and Zr ions
Trichloroacetic acid	$  \begin{array}{c}  Cl \quad O \\    \quad    \\  Cl - C - C - OH \\    \\  Cl  \end{array}  $	Will precipitate Ba, Ra, and the rare earths

## CHAPTER 13

# Solution Properties

### CONTENTS

Physical Properties of Liquid Water  
Refractive Index of Water  
Approximate pK Values of Compounds Useful in Buffer Systems  
Preparation of Buffers  
Dielectric Constants of Inorganic Solvents  
Dielectric Constants of Methanol–Water Mixtures from 5 to 55°C  
Common Drying Agents for Organic Liquids  
Common Recrystallization Solvents



## PHYSICAL PROPERTIES OF LIQUID WATER

The table below provides data on the most important properties of pure water under different temperatures. These properties are density (g/ml), molar volume (ml/mol), vapor pressure (in kPa and mmHg), static dielectric constant, and dynamic viscosity (mPa·sec). The properties other than the vapor pressure are evaluated at a pressure of 101.325 kPa or the vapor pressure, whichever is higher.

The properties were computed by a software implementation<sup>1</sup> of standards adopted by the International Association for the Properties of Water and Steam (IAPWS).<sup>2</sup>

## REFERENCES

1. Harvey, A.H., Peskin, A.P., and Klein, S.A., *NIST/ASME Steam Properties*, NIST Standard Reference Database 10, Version 2.2, National Institute of Standards and Technology, Gaithersburg, MD, 2000.
2. Documentation of IAPWS standards is available at [www.iapws.org](http://www.iapws.org).

Physical Properties of Liquid Water

Temperature (°C)	Density (g/ml)	Molar Volume (ml/mol)	Vapor Pressure (mmHg)	Vapor Pressure (kPa)	Dielectric Constant	Viscosity (mPa·sec)
0	0.99984	18.0181	4.584	0.6112	87.903	1.792
5	0.99997	18.0159	6.545	0.8726	85.916	1.518
10	0.99970	18.0206	9.212	1.228	83.975	1.306
15	0.99910	18.0314	12.794	1.706	82.078	1.138
18	0.99860	18.0405	15.487	2.065	80.960	1.053
20	0.99821	18.0476	17.546	2.339	80.223	1.002
25	0.99705	18.0686	23.776	3.170	78.408	0.8901
30	0.99565	18.0940	31.855	4.247	76.634	0.7973
35	0.99403	18.1234	42.221	5.629	74.898	0.7193
40	0.99222	18.1566	55.391	7.385	73.201	0.6530
45	0.99021	18.1933	71.968	9.595	71.540	0.5961
50	0.98804	18.2334	92.646	12.352	69.916	0.5468
55	0.98569	18.2768	118.22	15.762	68.328	0.5040
60	0.98320	18.3232	149.61	19.946	66.774	0.4664
65	0.98055	18.3726	187.83	25.042	65.256	0.4333
70	0.97776	18.4250	234.02	31.201	63.770	0.4039
75	0.97484	18.4802	289.49	38.595	62.318	0.3777
80	0.97179	18.5382	355.63	47.414	60.898	0.3543
85	0.96861	18.5991	434.03	57.867	59.509	0.3333
90	0.96531	18.6627	526.40	70.182	58.152	0.3144
95	0.96189	18.7291	634.61	84.608	56.825	0.2973
100	0.95835	18.7982	760.69	101.42	55.527	0.2817

## REFRACTIVE INDEX OF WATER

The following table provides the refractive index of liquid water at various temperatures.<sup>1</sup>

### REFERENCES

1. Lide, D.R., Ed., *CRC Handbook of Chemistry and Physics*, 83rd ed., CRC Press, Boca Raton, FL, 2002.

Refractive Index of Water	
Temperature, °C	Refractive Index, $n_d$ , Na d Line
15	1.33341
20	1.33299
30	1.33192
40	1.33051
50	1.32894
60	1.32718
70	1.32511
80	1.32287
90	1.32050
100	1.31783

## APPROXIMATE pK VALUES OF COMPOUNDS USEFUL IN BUFFER SYSTEMS

The following table provides the pK values of acids and bases needed to make the most popular buffers.<sup>1,2</sup> The approximate composition of buffers can be calculated from the equation

$$\text{pH} = \text{pK} + \log\{[\text{salt}]/[\text{acid}]\}$$

Note that the quantities in square brackets denote concentrations, and the logarithmic quantity refers to the common (base 10) logarithm.

## REFERENCES

1. Ramette, R.W., *Chemical Equilibrium and Analysis*, Addison-Wesley, Reading, MA, 1981.
2. Skoog, D.A., West, D.M., and Holler, F.J., *Analytical Chemistry: An Introduction*, 6th ed., Saunders, Philadelphia, 1994.

Approximate pK Values of Compounds Useful in Buffer Systems

pKa	Compound	Formula
2.12	(k <sub>1</sub> ) phosphoric acid	H <sub>3</sub> PO <sub>4</sub>
2.35	(k <sub>1</sub> ) glycine	H <sub>2</sub> NCH <sub>2</sub> CO <sub>2</sub> H
2.95	(k <sub>1</sub> ) phthalic acid	C <sub>6</sub> H <sub>4</sub> -1,2-(CO <sub>2</sub> H) <sub>2</sub>
3.22	(k <sub>1</sub> ) citric acid	HOC(COOH)(CH <sub>2</sub> COOH) <sub>2</sub>
3.66	(k <sub>1</sub> ) β,β'-dimethyl glutamic acid	[HO <sub>2</sub> CCH <sub>2</sub> ] <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub>
4.21	(k <sub>1</sub> ) succinic acid	HO <sub>2</sub> CCH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> H
4.76	acetic acid	CH <sub>3</sub> CO <sub>2</sub> H
4.84	(k <sub>2</sub> ) citric acid	HOC(COOH)(CH <sub>2</sub> COOH) <sub>2</sub>
5.41	(k <sub>2</sub> ) phthalic acid	C <sub>6</sub> H <sub>4</sub> -1,2-(CO <sub>2</sub> H) <sub>2</sub>
5.64	(k <sub>2</sub> ) succinic acid	HO <sub>2</sub> CCH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> H
6.4	(k <sub>1</sub> ) carbonic acid	H <sub>2</sub> CO <sub>3</sub>
6.15	(k <sub>1</sub> ) cacodylic acid	(CH <sub>3</sub> ) <sub>2</sub> As(O)OH
6.2	(k <sub>2</sub> ) β,β'-dimethyl glutaric acid	[HO <sub>2</sub> CCH <sub>2</sub> ] <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub>
6.33	(k <sub>2</sub> ) maleic acid	HO <sub>2</sub> CCH=CHCO <sub>2</sub> H
6.39	(k <sub>3</sub> ) citric acid	HOC(COOH)(CH <sub>2</sub> COOH) <sub>2</sub>
7.21	(k <sub>2</sub> ) phosphoric acid	H <sub>3</sub> PO <sub>4</sub>
8.07	(k <sub>1</sub> ) tris-(hydroxymethyl)-aminomethane	(HOCH <sub>2</sub> ) <sub>3</sub> CNH <sub>2</sub>
8.67	(k <sub>1</sub> ) 2-amino-2-methyl-1,3-propanediol	(HOCH <sub>2</sub> ) <sub>2</sub> C(CH <sub>3</sub> )NH <sub>2</sub>
9.23	(k <sub>1</sub> ) boric acid	H <sub>3</sub> BO <sub>3</sub>
9.78	(k <sub>2</sub> ) glycine	H <sub>2</sub> NCH <sub>2</sub> CO <sub>2</sub> H
10.33	(k <sub>2</sub> ) carbonic acid	H <sub>2</sub> CO <sub>3</sub>
12.32	(k <sub>3</sub> ) phosphoric acid	H <sub>3</sub> PO <sub>4</sub>

## PREPARATION OF BUFFERS

The following table gives the necessary information for preparing various buffers at different pH values. These buffers are suitable for use in either enzymatic or histochemical studies.<sup>1,2</sup> The accuracy of the tables is within  $\pm 0.05$  units of pH at 23°C, and the pH values do not change considerably even at 37°C. The recommended mixture of the various solutions is given under the corresponding pH with the final solution volume indicated. This assumes addition of water to the necessary dilution. A list of stock solutions follows the buffer/pH table. The approximate composition of buffers can be calculated from the equation

$$\text{pH} = \text{pK} + \log\{[\text{salt}]/[\text{acid}]\}$$

Note that the quantities in square brackets denote concentrations, and the logarithmic quantity refers to the common (base 10) logarithm.

## REFERENCES

1. Colowick, S.P. and Kaplan, N.O., Eds., *Methods in Enzymology*, Vol. 1, Academic Press, New York, 1955.
2. Perrin, D.D. and Dempsey, B., *Buffers for pH and Metal Ion Control*, Chapman & Hall, London, 1974.

**Preparation of Buffers (continued)**

Buffer	pH					Final Solution Volume
	3.0	3.1	3.2	3.3	3.4	
Glycine/hydrochloric acid	50.0 ml C + 11.4 ml B		50.0 ml C + 8.2 ml B		50.0 ml C + 6.4 ml B	200 ml
Phthalate/hydrochloric acid	50.0 ml D + 20.3 ml B		50.0 ml D + 14.7 ml B		50.0 ml D + 9.9 ml B	200 ml
Aconitate	20.0 ml E + 32.0 ml F	20.0 ml E + 36.0 ml F	20.0 ml E + 40.0 ml F	20.0 ml E + 44.0 ml F	20.0 ml E + 48.0 ml F	200 ml
Citrate	46.5 ml G + 3.5 ml H		43.7 ml G + 6.3 ml H		40.0 ml G + 10.0 ml H	100 ml
Citrate/phosphate	39.8 ml G + 10.2 ml K		37.7 ml G + 12.3 ml K		35.9 ml G + 14.1 ml K	100 ml
	pH					
	3.5	3.6	3.7	3.8	3.9	
Glycine/hydrochloric acid		50.0 ml C + 5.0 ml B				200 ml
Phthalate/hydrochloric acid		5.0 ml D + 6.0 ml B		50.0 ml D + 2.63 ml B		200 ml
Aconitate	20.0 ml E + 52.0 ml F	20.0 ml E + 56.0 ml F	20.0 ml E + 60.0 ml F	20.0 ml E + 64.0 ml F	20.0 ml E + 68.0 ml F	200 ml
Citrate		37.0 ml G + 13.0 ml H		35.0 ml G + 15.0 ml H		100 ml
Acetate		46.3 ml I + 3.7 ml J		44.0 ml I + 6.0 ml J		100 ml
Citrate/phosphate		33.9 ml G + 16.1 ml K		32.3 ml G + 17.7 ml K		100 ml
Succinate				25.0 ml L + 7.5 ml F		100 ml
	pH					
	4.0	4.1	4.2	4.3	4.4	
Aconitate	20.0 ml E + 72.0 ml F	20.0 ml E + 76.0 ml F	20.0 ml E + 79.6 ml F	20.0 ml E + 83.0 ml F	20.0 ml E + 86.6 ml F	200 ml
Citrate	33.0 ml G + 17.0 ml H		31.5 ml G + 18.5 ml H		28.0 ml G + 22.0 ml H	100 ml

Acetate	41.0 ml I + 9.0 ml J	36.8 ml I + 13.2 ml J	30.5 ml I + 19.5 ml J	100 ml
Citrate/phosphate	30.7 ml G + 19.3 ml K	29.4 ml G + 20.6 ml K	27.8 ml G + 22.2 ml K	100 ml
Succinate	25.0 ml L + 10.0 ml F	25.0 ml L + 13.3 ml F	25.0 ml L + 16.7 ml F	100 ml
Phthalate/sodium hydroxide		50.0 ml D + 3.7 ml F	50.0 ml D + 7.5 ml F	200 ml

pH					
	4.5	4.6	4.7	4.8	4.9
Aconitate	20.0 ml E + 90.0 ml F	20.0 ml E + 93.6 ml F	20.0 ml E + 97.0 ml F	20.0 ml E + 100.0 ml F	20.0 ml E + 103.0 ml F
Citrate		25.5 ml G + 24.5 ml H		23.0 ml G + 27.0 ml H	
Acetate		25.5 ml I + 24.5 ml J		20.0 ml I + 30.0 ml J	
Citrate/phosphate		26.7 ml G + 23.3 ml K		25.2 ml G + 24.8 ml K	
Succinate		25.0 ml L + 20.0 ml F		25.0 ml L + 23.5 ml F	
Phthalate/sodium hydroxide		50.0 ml D + 12.2 ml F		50.0 ml D + 17.7 ml F	

pH					
	5.0	5.1	5.2	5.3	5.4
Aconitate	20.0 ml E + 105.6 ml F	20.8 ml E + 108.0 ml F	20.0 ml E + 110.6 ml F	20.0 ml E + 113.0 ml F	20.0 ml E + 116.0 ml F
Citrate	20.5 ml G + 29.5 ml H		18.0 ml G + 32.0 ml H		16.0 ml G + 34.0 ml H
Acetate	14.8 ml I + 35.2 ml J		10.5 ml I + 39.5 ml J		8.8 ml I + 41.2 ml J
Citrate/phosphate	24.3 ml G + 25.7 ml K		23.3 ml G + 26.7 ml K		22.2 ml G + 27.8 ml K
Succinate	25.0 ml L + 26.7 ml F		25.0 ml L + 30.3 ml F		25.0 ml L + 34.2 ml F

*Note:* A list of the stock solutions follows the buffer table.

**Preparation of Buffers (continued)**

Buffer	pH					Final Solution Volume
	5.0	5.1	5.2	5.3	5.4	
Phthalate/sodium hydroxide	50.0 ml D + 23.9 ml F		50.0 ml D + 30.0 ml F		50.0 ml D + 35.5 ml F	200 ml
Maleate			50.0 ml M + 7.2 ml F		50.0 ml M + 10.5 ml F	200 ml
Cacodylate	50.0 ml N + 47.0 ml B		50.0 ml N + 45.0 ml B		50.0 ml N + 43.0 ml B	200 ml
Tris-maleate			50.0 ml Q + 7.0 ml F		50.0 ml Q + 10.8 ml F	200 ml
	pH					
	5.5	5.6	5.7	5.8	5.9	
Aconitate	20.0 ml E + 119.0 ml F	20.0 ml E + 122.6 ml F	20.0 ml E + 126.0 ml F			200 ml
Citrate		13.7 ml G + 36.3 ml H		11.8 ml G + 38.2 ml H		100 ml
Acetate		4.8 ml I + 45.2 ml J				100 ml
Citrate/phosphate		21.0 ml G + 29.0 ml K		19.7 ml G + 30.3 ml K		100 ml
Succinate		25.0 ml L + 37.5 ml F		25.0 ml L + 40.7 ml F		100 ml
Phthalate/sodium hydroxide		50.0 ml D + 39.8 ml F		50.0 ml D + 43.0 ml F		200 ml
Maleate		50.0 ml M + 15.3 ml F		50.0 ml M + 20.8 ml F		200 ml
Cacodylate		50.0 ml N + 39.2 ml B		50.0 ml N + 34.8 ml B		200 ml
Phosphate			93.5 ml O + 6.5 ml P	92.0 ml O + 8.0 ml P	90.0 ml O + 10.0 ml P	200 ml
Tris-maleate		50.0 ml Q + 15.5 ml F		50.0 ml Q + 20.5 ml F		200 ml

		pH				
		6.0	6.1	6.2	6.3	6.4
Citrate	9.5 ml G + 41.5 ml H			7.2 ml G + 42.8 ml H		100 ml
Citrate/phosphate	17.9 ml G + 32.1 ml K			16.9 ml G + 33.1 ml K	15.4 ml G + 34.6 ml K	100 ml
Succinate	25.0 ml L + 43.5 ml F					100 ml
Phthalate/sodium hydroxide	50.0 ml D + 45.5 ml F					200 ml
Maleate	50.0 ml M + 26.9 ml F			50.0 ml M + 33.0 ml F	50.0 ml M + 38.0 ml F	200 ml
Cacodylate	50.0 ml N + 29.6 ml B			50.0 ml N + 23.8 ml B	50.0 ml N + 18.3 ml B	200 ml
Phosphate	87.7 ml O + 12.3 ml P	85.0 ml O + 15.0 ml P		81.5 ml O + 18.5 ml P	77.5 ml O + 22.5 ml P	200 ml
Tris-maleate	50.0 ml Q + 26.0 ml F			50.0 ml Q + 31.5 ml F	50.0 ml Q + 37.0 ml F	200 ml
		pH				
		6.5	6.6	6.7	6.8	6.9
Barbital					50.0 ml R + 45.0 ml B	200 ml
Citrate/phosphate			13.6 ml G + 36.4 ml K		9.1 ml G + 40.9 ml K	100 ml
Maleate			50.0 ml M + 41.6 ml F		50.0 ml M + 44.4 ml F	200 ml
Cacodylate			40.0 ml N + 13.3 ml B		50.0 ml N + 9.3 ml B	200 ml
Phosphate	68.5 ml O + 31.5 ml P	62.5 ml O + 37.5 ml P		56.5 ml O + 43.5 ml P	51.0 ml O + 49.0 ml P	200 ml
Tris-maleate			50.0 ml Q + 42.5 ml F		50.0 ml Q + 45.0 ml F	200 ml

*Note:* A list of the stock solutions follows the buffer table.



**Preparation of Buffers (continued)**

Buffer	pH					Final Solution Volume
	7.0	7.1	7.2	7.3	7.4	
Barbital	50.0 ml R + 43.0 ml B		50.0 ml R + 39.0 ml B		50.0 ml R + 32.5 ml B	200 ml
Tris			50.0 ml S + 44.2 ml B		50.0 ml S + 41.4 ml B	200 ml
Citrate/phosphate	6.5 ml G + 43.6 ml K					100 ml
Cacodylate	50.0 ml N + 6.3 ml B		50.0 ml N + 4.2 ml B		50.0 ml N + 2.7 ml B	200 ml
Phosphate	39.0 ml O + 61.0 ml P	33.0 ml O + 67.0 ml P	28.0 ml O + 72.0 ml P	23.0 ml O + 77.0 ml P	19.0 ml O + 81.0 ml P	200 ml
Tris-maleate	50.0 ml Q + 48.0 ml F		50.0 ml Q + 51.0 ml F		50.0 ml Q + 54.0 ml F	200 ml
	pH					
	7.5	7.6	7.7	7.8	7.9	
Barbital		50.0 ml R + 27.5 ml B		50.0 ml R + 22.5 ml B		200 ml
Tris		50.0 ml S + 38.4 ml B		50.09 ml S + 32.5 ml B		200 ml
Boric acid/borax		50.0 ml T + 2.0 ml U		50.0 ml T + 3.1 ml U		200 ml
Ammediol				50.0 ml V + 43.5 ml B		200 ml
Phosphate	16.0 ml O + 84.0 ml P	13.0 ml O + 87.0 ml P	10.5 ml O + 90.5 ml P	8.5 ml O + 91.5 ml P	7.0 ml O + 93.0 ml P	200 ml
Tris-maleate		50.0 ml Q + 58.0 ml F		50.0 ml Q + 63.5 ml F		200 ml
	pH					
	8.0	8.1	8.2	8.3	8.4	
Barbital	50.0 ml R + 17.5 ml B		50.0 ml R + 12.7 ml B		50.0 ml R + 9.0 ml B	200 ml
Tris	50.0 ml S + 26.8 ml B		50.0 ml S + 21.9 ml B		50.0 ml S + 16.5 ml B	200 ml

Boric acid/borax	50.0 ml T + 4.9 ml U	50.0 ml T + 7.3 ml U	50.0 ml T + 11.5 ml U	200 ml
Ammediol	50.0 ml V + 41.0 ml B	50.0 ml V + 37.7 ml B	50.0 ml V + 34.0 ml B	200 ml
Phosphate	5.3 ml O + 94.7 ml P			200 ml
Tris-maleate	50.0 ml Q + 69.0 ml F	50.0 ml Q + 75.0 ml F	50.0 ml Q + 81.0 ml F	200 ml

pH					
8.5	8.6	8.7	8.8	8.9	
Barbital	50.0 ml R + 6.0 ml B		50.0 ml R + 4.0 ml B		200 ml
Tris	50.0 ml S + 12.2 ml B		50.0 ml S + 8.1 ml B		200 ml
Boric acid/borax	50.0 ml T + 17.5 ml U	50.0 ml T + 22.5 ml U	50.0 ml T + 30.0 ml U	50.0 ml T + 42.5 ml U	200 ml
Ammediol	50.0 ml V + 29.5 ml B		50.0 ml V + 22.0 ml B		200 ml
Glycine/sodium hydroxide	50.0 ml C + 4.0 ml F		50.0 ml C + 6.0 ml F		200 ml
Tris-maleate	50.0 ml Q + 86.5 ml F				200 ml

pH					
9.0	9.1	9.2	9.3	9.4	
Barbital	50.0 ml R + 2.5 ml B	50.0 ml R + 1.5 ml B			200 ml
Tris	50.0 ml S + 5.0 ml B				200 ml
Boric acid/borax	50.0 ml T + 59.0 ml U	50.0 ml T + 83.0 ml U	50.0 ml T + 115.0 ml U		200 ml
Ammediol	50.0 ml V + 16.7 ml B	50.0 ml V + 12.5 ml B		50.0 ml V + 8.5 ml B	200 ml
Glycine/sodium hydroxide	50.0 ml C + 8.8 ml F	50.0 ml C + 12.0 ml F		50.0 ml C + 16.8 ml F	200 ml

*Note:* A list of the stock solutions follows the buffer table.

**Preparation of Buffers (continued)**

Buffer	pH					Final Solution Volume
	9.0	9.1	9.2	9.3	9.4	
Borax/sodium hydroxide			50.0 ml U (pH = 9.28)		50.0 ml U + 11.0 ml F	200 ml
Carbonate/bicarbonate			4.0 ml W + 46.0 ml X	7.5 ml W + 42.5 ml X	9.5 ml W + 40.5 ml X	200 ml
	pH					
	9.5	9.6	9.7	9.8	9.9	
Ammediol		50.0 ml V + 5.7 ml B		50.0 ml V + 3.7 ml B		200 ml
Glycine/sodium hydroxide		50.0 ml C + 22.4 ml F		50.0 ml C + 27.2 ml F		200 ml
Borax/sodium hydroxide	50.0 ml U + 17.6 ml F	50.0 ml U + 23.0 ml F	50.0 ml U + 29.0 ml F	50.0 ml U + 34.0 ml F	50.0 ml U + 38.0 ml F	200 ml
Carbonate/bicarbonate	13.0 ml W + 37.0 ml X	16.0 ml W + 34.0 ml X	19.5 ml W + 30.5 ml X	22.0 ml W + 28.0 ml X	25.0 ml W + 25.0 ml X	200 ml
	pH					
	10.0	10.1	10.2	10.3	10.4	
Ammediol	50.0 ml V + 2.0 ml B					200 ml
Glycine/sodium hydroxide	50.0 ml C + 32.0 ml F				50.0 ml C + 45.5 ml F	200 ml
Borax/sodium hydroxide	50.0 ml U + 43.0 ml F	50.0 ml U + 46.0 ml F				200 ml
Carbonate/bicarbonate	27.5 ml W + 22.5 ml X	30.0 ml W + 20.0 ml X	33.0 ml W + 17.0 ml X	35.5 ml W + 14.5 ml X	38.5 ml W + 11.5 ml X	200 ml
	pH					
	10.5	10.6	10.7	10.8	10.9	
Glycine/sodium hydroxide		50.0 ml C + 45.5 ml F				200 ml
Carbonate/bicarbonate	40.5 ml W + 9.5 ml X	42.5 ml W + 7.5 ml X	45.0 ml W + 5.0 ml X			200 ml

*Note:* A list of the stock solutions follows the buffer table.

## Stock Solutions

A	=	0.2 <i>M</i> potassium chloride (14.91 g in 1000 ml)
B	=	0.2 <i>M</i> hydrochloric acid
C	=	0.2 <i>M</i> glycine (15.01 g in 1000 ml)
D	=	0.2 <i>M</i> potassium acid phthalate (40.84 g in 1000 ml)
E	=	0.5 <i>M</i> aconitic acid, 1-propene-1,2,3-tricarboxylic acid (87.05 g in 1000 ml)
F	=	0.2 <i>M</i> sodium hydroxide
G	=	0.1 <i>M</i> citric acid (21.01 g in 1000 ml)
H	=	0.1 <i>M</i> sodium citrate dihydrate (29.41 g in 1000 ml); avoid using any other hydrated salt
I	=	0.2 <i>M</i> acetic acid
J	=	0.2 <i>M</i> anhydrous sodium acetate (16.4 g in 1000 ml) or 0.2 <i>M</i> sodium acetate trihydrate (27.2 g in 1000 ml)
K	=	0.2 <i>M</i> dibasic sodium phosphate heptahydrate (53.65 g in 1000 ml) or 0.2 <i>M</i> dibasic sodium phosphate dodecahydrate (71.7 g in 1000 ml)
L	=	0.2 <i>M</i> succinic acid (23.6 g in 1000 ml)
M	=	0.2 <i>M</i> sodium maleate (8.0 g of NaOH + 23.2 g of maleic acid or 19.6 g of maleic anhydride in 1000 ml)
N	=	0.2 <i>M</i> sodium cacodylate (42.8 g of sodium cacodylate trihydrate in 1000 ml)
O	=	0.2 <i>M</i> monobasic sodium phosphate (27.8 g in 1000 ml)
P	=	0.2 <i>M</i> dibasic sodium phosphate (53.65 g of dibasic sodium phosphate heptahydrate or 71.7 g of dibasic sodium phosphate dodecahydrate in 1000 ml)
Q	=	0.2 <i>M</i> tris acid maleate (24.2 g of tris (hydroxymethyl) amino methane + 23.2 g of maleic acid or 19.6 g of maleic anhydride in 1000 ml)
R	=	0.2 <i>M</i> sodium barbital (veronal) (41.2 g in 1000 ml)
S	=	0.2 <i>M</i> tris (hydroxymethyl) aminomethane (24.2 g in 1000 ml)
T	=	0.2 <i>M</i> boric acid (12.4 g in 1000 ml)
U	=	0.05 <i>M</i> borax (19.05 g in 1000 ml)
V	=	0.2 <i>M</i> 2-amino-2-methyl-1,3-propanediol (21.03 g in 1000 ml)
W	=	0.2 <i>M</i> anhydrous sodium carbonate (21.2 g in 1000 ml)
X	=	0.2 <i>M</i> anhydrous sodium bicarbonate (16.8 g in 1000 ml)

## DIELECTRIC CONSTANTS OF INORGANIC SOLVENTS

The dielectric constant ( $\epsilon$ ) of a substance is a macroscopic property that measures the reduction of the strength of the electric field that surrounds a charged particle when immersed in that substance, as compared to the field strength around the same particle when placed in a vacuum. As a result, the higher the value of the dielectric constant of the substance, the greater the tendency of the charged particle to ionize. Although the dielectric constant gives only one of several quantitative measures of the polarity of the substance, it is nonetheless a useful property in describing solvents as polar or nonpolar. The table below lists the dielectric constants of some inorganic solvents at specific temperatures.<sup>1-3</sup>

## REFERENCES

1. Lide, D.R., Ed., *CRC Handbook of Chemistry and Physics*, 83rd ed., CRC Press, Boca Raton, FL, 2002.
2. Lowry, T.H. and Richardson, K.S., *Mechanism and Theory in Organic Chemistry*, Harper Collins Publishers, New York, 1987.
3. Parsons, R., *Handbook of Electrochemical Constants*, Butterworths, London, 1959.

### Dielectric Constants of Inorganic Solvents

Name	Formula	Dielectric Constant ( $\epsilon$ )	Temperature (°C)
Aluminum bromide	AlBr <sub>3</sub>	3.38	100
Ammonia	NH <sub>3</sub>	16.9	25
Argon	Ar	1.53	−191
Arsenic trichloride	AsCl <sub>3</sub>	12.8	20
Arsine	AsH <sub>3</sub>	2.50	−100
Boron tribromide	BBr <sub>3</sub>	2.58	0
Bromine	Br <sub>2</sub>	3.09	20
Chlorine	Cl <sub>2</sub>	2.10	−50
Deuterium	D <sub>2</sub>	1.277	−253
Deuterium oxide (see water-d <sub>2</sub> )			
Dinitrogen tetroxide	N <sub>2</sub> O <sub>4</sub>	2.4	18
Fluorine	F <sub>2</sub>	1.54	−202
Germanium tetrachloride	GeCl <sub>4</sub>	2.43	25
Helium	He	1.055	−271
Hydrazine	N <sub>2</sub> H <sub>4</sub>	51.7	25
Hydrogen bromide	HBr	7.0	−70
Hydrogen chloride	HCl	12.0	−113
Hydrogen cyanide	HCN	106.8	25
Hydrogen fluoride	HF	17.0	−73
		83.6	25
Hydrogen iodide	HI	3.39	−50
Hydrogen peroxide	H <sub>2</sub> O <sub>2</sub>	84.2	0
Hydrogen sulfide	H <sub>2</sub> S	9.26	−85.5
Iodine	I <sub>2</sub>	11.1	118
Iodine pentafluoride	IF <sub>5</sub>	36.2	25
Lead tetrachloride	PbCl <sub>4</sub>	2.78	20
Mercury (II) bromide	HgBr <sub>2</sub>	9.8	240
Nitrosyl bromide	NOBr	13.4	15
Nitrosyl chloride	NOCl	18.2	12
Phosphorus trichloride	PCl <sub>3</sub>	3.43	25
Phosphorus pentachloride	PCl <sub>5</sub>	2.8	160
Phosphoryl chloride	POCl <sub>3</sub>	13.3	22
Selenium	Se	5.40	250
Seleninyl chloride	SeOCl <sub>2</sub>	26.2	20
Silicon tetrachloride	SiCl <sub>4</sub>	2.40	20
Sulfur	S	3.52	118
Sulfur dioxide	SO <sub>2</sub>	14.1	20
Sulfuric acid	H <sub>2</sub> SO <sub>4</sub>	101	25
Sulfuryl chloride	SO <sub>2</sub> Cl <sub>2</sub>	9.2	20
Thionyl bromide	SOBr <sub>2</sub>	9.06	20
Thionyl chloride	SOCl <sub>2</sub>	9.25	20
Thiophosphoryl chloride	PSCl <sub>3</sub>	5.8	22
Titanium tetrachloride	TiCl <sub>4</sub>	2.80	20
Water	H <sub>2</sub> O	80.22	20
		78.41	25
Water-d <sub>2</sub>	D <sub>2</sub> O	77.94	25

## DIELECTRIC CONSTANTS OF METHANOL–WATER MIXTURES FROM 5 TO 55°C

The table below lists the value of dielectric constants of methanol–water mixtures as a function of their respective mass/mass% composition at various temperatures.<sup>1</sup> This information is useful for a variety of chromatographic and extractive applications.

### REFERENCES

1. Parsons, R., *Handbook of Electrochemical Constants*, Butterworths, London, 1959.

**Dielectric Constants of Methanol–Water Mixtures from 5 to 55°C**

<b>Mass% Methanol</b>	<b>5°C</b>	<b>15°C</b>	<b>25°C</b>	<b>35°C</b>	<b>45°C</b>	<b>55°C</b>
0	85.76	83.83	78.30	74.83	71.51	68.35
10	81.68	77.83	74.18	70.68	67.32	64.08
20	77.38	73.59	69.99	66.52	63.24	60.06
30	72.80	69.05	65.55	62.20	58.97	55.92
40	67.91	64.31	60.94	57.72	54.62	51.69
50	62.96	59.54	56.28	53.21	50.29	47.53
60	57.92	54.71	51.67	48.76	46.02	43.42
70	52.96	49.97	47.11	44.42	41.83	39.38
80	48.01	45.24	42.60	40.08	37.70	35.46
90	42.90	40.33	37.91	35.65	33.53	31.53
95	39.98	37.61	35.38	33.28	31.29	29.43
100	36.88	34.70	32.66	30.74	28.02	27.21

## COMMON DRYING AGENTS FOR ORGANIC LIQUIDS

The following table gives the suggested common agents for drying various organic liquids. Those squares marked “X” are the best combination of organic family/drying agent. Those marked “never” are the worst combinations, primarily due to possible chemical reactions. For instance, alcohols and sodium metal react vigorously. Consequently, one should look for other drying agents. Those that are blank might be efficient, but are not recommended for use, unless the suggested drying agents are not available. Some combinations do not give efficient results due to complexation (marked “d”).<sup>1-6</sup>

## REFERENCES

1. Vogel, A.I., *A Textbook of Practical Organic Chemistry*, Longmans, Green and Co., London, 1951.
2. Brewster, R.Q., Vanderwerf, C.A., and McEwen, W.E., *Unitized Experiments in Organic Chemistry*, D. Van Nostrand Co., New York, 1977.
3. Gordon, A.J. and Ford, R.A., *The Chemist's Companion: A Handbook of Practical Data, Techniques and References*, John Wiley & Sons, New York, 1972.
4. Bruno, T.J. and Svoronos, P.D.N., *Basic Tables for Chemical Analysis*, NBS Technical Note 1096, U.S. Dept. of Commerce, National Bureau of Standards, Washington, D.C., 1986.
5. Bruno, T.J. and Svoronos, P.D.N., *CRC Handbook of Basic Tables for Chemical Analysis*, CRC Press, Boca Raton, FL, 1989.
6. Sarlo, E., Svoronos, P.D.N., and Kulawec, R., *Organic Chemistry Laboratory Manual*, 2nd ed., W.C. Brown, Dubuque, IA, 1997.

Common Drying Agents for Organic Liquids

Family	Na <sub>2</sub> CO <sub>3</sub> <sup>a</sup>	K <sub>2</sub> CO <sub>3</sub> <sup>a</sup>	MgSO <sub>4</sub> <sup>b</sup>	CaSO <sub>4</sub> <sup>c</sup>	Na <sub>2</sub> SO <sub>4</sub> <sup>c</sup>	CaCl <sub>2</sub>
Alcohols		X	X	X		d
Aldehydes			X	X	X	d
Alkyl halides						X
Amines						d
Anhydrides						
Aryl halides						X
Carboxylic acids	Never	Never	X	X	X	e
Esters			X		X	d
Ethers				X		X
Hydrocarbons, aromatic	X	X		X	Poor	X
Hydrocarbons, saturated	X	X		X	Poor	X
Hydrocarbons, unsaturated	X	X			Poor	X
Ketones		X	X	X	X	d
Nitriles						

<sup>a</sup> Excellent for salting out.

<sup>b</sup> Best all-purpose drying agent.

<sup>c</sup> High capacity, but slow reacting.

<sup>d</sup> Forms complexes.

<sup>e</sup> Lime (common impurity) reacts with acidic hydrogen.



**Common Drying Agents for Organic Liquids (continued)**

<b>Family</b>	<b>Na</b>	<b>P<sub>2</sub>O<sub>5</sub></b>	<b>NaOH (solid)</b>	<b>KOH (solid)</b>	<b>CaO</b>	<b>CaH<sub>2</sub></b>	<b>LiAlH<sub>4</sub></b>
Alcohols	Never	Never	Never	Never	X	g	Never
Aldehydes	Never	Never	Never	Never		Never	Never
Alkyl halides	Never	X	Never	Never		X	Never
Amines	Never	Never	X	X	X	f	Never
Anhydrides		X					
Aryl halides	Never	X				X	X
Carboxylic acids	Never	X	Never	Never	Never	Never	Never
Esters			Never	Never		X	Never
Ethers	X	X			X	X	X
Hydrocarbons, aromatic	X	X				X	X
Hydrocarbons, saturated	X	X				X	X
Hydrocarbons, unsaturated		X				X	X
Ketones	Never	Never	Never	Never	Never	Never	Never
Nitriles		X	Never	Never			Never

<sup>a</sup> Excellent for salting out.

<sup>b</sup> Best all-purpose drying agent.

<sup>c</sup> High capacity, but slow reacting.

<sup>d</sup> Forms complexes.

<sup>e</sup> Lime (common impurity) reacts with acidic hydrogen.

<sup>f</sup> Only for 3° amines (R<sub>3</sub>N).

<sup>g</sup> Only for C<sub>4</sub> and higher alcohols.

## COMMON RECRYSTALLIZATION SOLVENTS

The following table gives a list of solvents (and their useful properties) in order of decreasing polarity, and the organic compounds they are capable of recrystallizing. In choosing a solvent, one should consider the following criteria: (1) low toxicity; (2) low cost; (3) ease of separation of the solvent from the crystals (relatively high degree of volatility); (4) the ability to dissolve the crystals while hot, but not while cold, with impurities being either soluble or insoluble in both hot and cold; and (5) the boiling point of the solvent should be lower than the melting point of the compound. Although not all of these factors may be optimized with each application, an attempt should be made to achieve optimization of as many as possible. For the same compound, a variety of recrystallizing solvents can be employed based on the type of impurities that are present.<sup>1-4</sup>

## REFERENCES

1. Gordon, A.J. and Ford, R.A., *The Chemist's Companion: A Handbook of Practical Data, Techniques, and References*, John Wiley & Sons, New York, 1972.
2. Roberts, R.M., Gilbert, J.C., Rodewald, L.B., and Wingrove, A.S., *An Introduction to Modern Experimental Organic Chemistry*, Holt, Rinehart, and Winston, New York, 1969.
3. Sarlo, E., Svoronos, P.D.N., and Kulawec, R., *Organic Chemistry Laboratory Manual*, 2nd ed., W.C. Brown, Dubuque, IA, 1997.
4. Lide, D.R., Ed., *CRC Handbook of Chemistry and Physics*, 83rd ed., CRC Press, Boca Raton, FL, 2002.

### Common Recrystallization Solvents

Solvent	bp <sup>a</sup> (°C)	ε <sup>b,c</sup>	Flammability <sup>e</sup>	Toxicity	Good for	Second Solvent in Mixture <sup>d</sup>	Comments
Water	100	78.5 <sup>c</sup>	0	0	Amides, salts, some carboxylic acids	Methanol, ethanol, acetone, dioxane, acetonitrile	Difficult to remove from crystals
Acetic acid	118	6.15 <sup>b</sup>	1	2	Amides, some carboxylic acids, some sulfoxides	Water	Difficult to remove from crystals
Acetonitrile	81.6	37.5 <sup>b</sup>	3	3	Some carboxylic acids, hydroquinones	Water, ether, benzene	
Methanol	64.5	32.63 <sup>c</sup>	3	1	Nitro compounds, esters, bromo compounds, some sulfoxides, sulfones, sulfilimines, anilines	Water, ether, benzene	
Ethanol	78.3	24.30 <sup>c</sup>	3	0	Same as methanol	Water, ethyl acetate, hydrocarbons, methylene chloride	
Acetone	56	20.7 <sup>c</sup>	3	1	Nitro compounds, osazones	Water, ether, hydrocarbons	
2-Methoxyethanol (methyl cellosolve)	124		2	2	Carbohydrates	Water, ether, benzene	
Pyridine	116	123 <sup>c</sup>	3	3	Quinones, thiazoles, oxazoles	Water, methanol	Difficult to remove from crystals
Methyl acetate	57	6.68	4	2	Esters, carbonyl compounds, sulfide derivatives, carbinols	Water, ether	
Ethyl acetate	77.1	6.02 <sup>c</sup>	3	1	Same as methyl acetate	Water, ether, chloroform, methylene chloride	
Methylene chloride (dichloromethane)	40	9.08	0	2	Low-melting compounds	Ethanol, hydrocarbons	Easily removed
Ether (diethylether)	34.5	4.34 <sup>b</sup>	4	2	Low-melting compounds	Acetone, acetonitrile, methanol, ethanol, acetate esters	Easily removed; can create peroxides
Chloroform	61.7	4.81 <sup>b</sup>	0	4	Polar compounds	Ethanol, acetate, esters, hydrocarbons	Easily removed; suspected carcinogen <sup>f</sup>
Dioxane	102	2.21 <sup>c</sup>	3	2	Amides	Water, hydrocarbons, benzene	Can form complexes with ethers

Carbon tetrachloride	76.5	2.24 <sup>b</sup>	0	4	Acid chlorides, anhydrides	Ether, benzene, hydrocarbons	Can react with strong organic bases; suspected carcinogen <sup>f</sup>
Toluene	110.6	2.38 <sup>c</sup>	3	2	Aromatics, hydrocarbons	Ether, ethyl acetate, hydrocarbons	Somewhat difficult to remove from crystals
Benzene	80.1	2.28 <sup>b</sup>	3	3	Aromatics, hydrocarbons, molecular complexes, sulfides, ethers	Ether, ethyl acetate, hydrocarbons	Suspected carcinogen <sup>f</sup>
Ligroin (naphtha solvent)	90–110	—	3	1	Hydrocarbons, aromatic heterocycles	Ethyl acetate, benzene, methylene chloride	
Petroleum ether (ACS)	35–60	—	4	1	Hydrocarbons	Any solvent less polar than ethanol	Easy to separate
<i>n</i> -Pentane	36.1	1.84 <sup>b</sup>	4	1	Hydrocarbons	Any solvent less polar than ethanol	Easy to separate
<i>n</i> -Hexane	69	1.89 <sup>b</sup>	4	1	Hydrocarbons	Any solvent less polar than ethanol	
Cyclohexane	80.7	2.02 <sup>b</sup>	4	1	Hydrocarbons	Any solvent less polar than ethanol	
<i>n</i> -Heptane	98.4	1.91 <sup>c</sup>	4	1	Hydrocarbons	Any solvent less polar than ethanol	

<sup>a</sup> Normal boiling point (°C).

<sup>b</sup> Dielectric constant (20°C).

<sup>c</sup> Dielectric constant (25°C).

<sup>d</sup> Second solvent used to facilitate dissolving the crystals in a solvent mixture.

<sup>e</sup> Scale varies from 4 (highly flammable, highly toxic) to 0 (not flammable, not toxic).

<sup>f</sup> See carcinogen table.

## CHAPTER 14

# Tables for Laboratory Safety

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## MAJOR CHEMICAL INCOMPATIBILITIES

The following chemicals react, sometimes violently (indicated by italics), in certain chemical environments.<sup>1-5</sup> Incompatibilities may cause fires, explosions, or the release of toxic gases. Extreme care must be taken when working with these materials. This list is not inclusive, and the reader is urged to consult multiple sources for more specific information.

## REFERENCES

1. Dean, J.A., Ed., *Lange's Handbook of Chemistry*, 15th ed., McGraw-Hill Book Company, New York, 1998.
2. Fieser, L.F. and Fieser, M., *Reagents for Organic Synthesis*, John Wiley & Sons, New York, 1967.
3. Gordon, A.J. and Ford, R.A., *The Chemist's Companion: A Handbook of Practical Data, Techniques and References*, John Wiley & Sons, New York, 1972.
4. Shugar, G.J. and Dean, J.A., *The Chemist's Ready Reference Handbook*, McGraw-Hill Book Company, New York, 1990.
5. Svoronos, P., Sarlo, E., and Kulaweic, R., *Organic Chemistry Laboratory Manual*, 2nd ed., McGraw-Hill Book Company, New York, 1997.

### Major Chemical Incompatibilities

Chemical	Incompatible Chemicals
Acetic acid	Strong acids (chromic, nitric, perchloric), peroxides
Acetylene	Air, copper, halogens (chlorine, bromine, iodine), <i>silver</i>
Alkali metals	<i>Acids, water, hydroxy compounds, polychlorinated hydrocarbons</i> (for example, $\text{CCl}_4$ ), halogens, carbon dioxide, oxidants
Ammonia, anhydrous	<i>Halogens (bromine, chlorine, iodine), hydrofluoric acid, liquid oxygen</i> , calcium or sodium hypochlorite, heavy metals (silver, gold, mercury), nitric acid
Ammonium nitrate	<i>Metal powders, chlorates, nitrites, sulfur, sugar</i> , flammable and combustible organics, acids, sawdust
Anilines	<i>Concentrated acids (nitric, chromic), oxidizing agents (chromium (III) ions, peroxides, permanganate)</i>
Carbon, activated	Oxidizing agents, unsaturated oils
Carboxylic acids	Metals ( <i>alkalis</i> ), organic bases, ammonia
Chlorates	<i>Flammable and combustible organic compounds</i> , finely powdered metals, manganese dioxide, ammonium salts
Chromic acid	<i>Anilines</i> , 1° or 2° alcohols
Halogens (chlorine, bromine)	<i>Finely powdered metals, diethyl ether, hydrogen</i> , unsaturated organic compounds, carbide salts, acetylene, alkali metal
Copper	Oxidizing agents
Ether (diethyl)	<i>Peroxides</i> (especially after long exposure of ether to air; see the other tables in this chapter dealing with this compound)
Fluorine	Reactive (as a strong oxidizing agent) to a certain degree with most compounds, but it can sometimes cause a violent reaction
Hydrocarbons (saturated)	Halogens (especially <i>fluorine</i> ) in the presence of ultraviolet light and peroxides
Hydrocarbons (unsaturated)	Halogens, concentrated strong acids, peroxides
Hydrofluoric acid	Ammonia, glass
Hydrogen peroxide	Metals, alcohols, potassium permanganate, flammable and combustible materials
Iodine	<i>Acetaldehyde, antimony</i> , unsaturated hydrocarbons, ammonia, and some amines
Mercury	Some metals, ammonia, terminal alkynes (see the other tables in this chapter dealing with this element)
Nitric acid (concentrated)	<i>Anilines, flammable liquids, unsaturated organics, lactic acid, coal</i> , ammonia, powdered metals, wood, alcohols, electron-rich aromatic rings (phenols, anilines)
Perchloric acid	Some organics, acetic anhydride, metals, alcohols, wood and its derivatives (see the other tables in this chapter dealing with this compound)
Permanganates, general	Aldehydes, alcohols, unsaturated hydrocarbons
Peroxides	<i>Flammable liquids, metals</i> , aldehydes, alcohols, impact, hydrocarbons (unsaturated)
Picric acid	<i>Dryness and impact, alkali metals, oxidizing agents</i> , concentrated bases
Potassium, metal	See alkali metals
Potassium permanganate	<i>Hydrochloric acid</i> , glycerol, hydrogen peroxide, sulfuric acid, wood
Silver salts, organic	<i>Dryness and prolonged air exposure</i>
Sodium, metal	See alkali metals
Sulfuric acid, concentrated	<i>Electron-rich aromatic rings (phenols, anilines), unsaturated hydrocarbons, potassium permanganate, chlorates, perchlorates</i>

## PROPERTIES OF HAZARDOUS SOLIDS

The following table lists some of the more important properties of hazardous room temperature solids commonly used in the analytical laboratory.<sup>1</sup> The flash points were determined with the open-cup method.

## REFERENCES

1. Turner, C.F. and McCreery, J.W., *The Chemistry of Fire and Hazardous Materials*, Allyn and Bacon, Boston, 1981.



**Properties of Hazardous Solids**

Name	Formula	Specific Gravity (at 20°C)	Melting Point, °C	Boiling Point, °C	Flash Point, °C	Autoignition Point, °C	Ignition/Explosion Mechanism	Fire Suppression Media
Acetyl peroxide	(CH <sub>3</sub> CO) <sub>2</sub> O <sub>2</sub>	1.2	30	63	—	—	Heat, shock	a, c
Adipic acid	(CH <sub>2</sub> ) <sub>4</sub> (COOH) <sub>2</sub>	1.3	152	330	196	420	Heat	a, b, c, d
Aluminum (finely divided)	Al	2.7	660	2270	—	—	Mixing with iron oxides	a
Aluminum chlorate	Al(ClO <sub>3</sub> ) <sub>3</sub>	—	—	—	—	—	Heat, impact agents, reducing agents	a
Aluminum chloride	AlCl <sub>3</sub>	2.4	192	180	—	—	Heat, moisture	a
Ammonium nitrate	NH <sub>4</sub> NO <sub>3</sub>	1.7	169	210	—	—	Heat	b
Ammonium nitrite	NH <sub>4</sub> NO <sub>2</sub>	1.7	dec	—	70	—	Heat, shock, impact	a
Ammonium perchlorate	NH <sub>4</sub> ClO <sub>4</sub>	—	dec	—	—	—	Shock, impact	—
Antimony	Sb	6.7	630	1375	—	—	Heat, water	a
Antimony trisulfide	SbS <sub>3</sub>	4.6	—	—	—	—	Heat, strong organic acids, oxidizers	b
Antimony pentasulfide	SbS <sub>5</sub>	4.1	—	—	—	—	Heat, strong oxidizers, acids	a
Barium	Ba	3.6	850	1530	—	—	Heat	a
Beryllium	Be	1.87	1280	1500	—	—	Heat, friction	a
Cadmium	Cd	8.6	321	765	—	—	Heat	a
Calcium hypochlorite	CaCl(ClO)·4H <sub>2</sub> O	—	dec	—	—	—	Heat, contact with combustible material, acid	—
Camphor	C <sub>10</sub> H <sub>16</sub> O	1.0	177	sub	66	466	High concentration in air	a, c
Cesium	Cs	1.9	29	670	—	—	Water	f
Iodine	I <sub>2</sub>	4.9	113	183	—	—	Heat	c
Lithium	Li	0.53	179	1335	—	—	Water, inorganic acids	a
Magnesium	Mg	1.75	651	1107	—	—	Water	a
Phosphorus, red	P <sub>4</sub>	2.2	600	sub	—	260	Heat, oxidizers	b, e
Phosphorus, white	P <sub>4</sub>	1.82	44	279	Ambient	30	Heat, oxidizers, dry atmosphere	b
Phosphorus pentachloride	PCl <sub>5</sub>	4.7	167	sub	—	—	Moist air, heat	a, c
Phosphorus pentasulfide	P <sub>2</sub> S <sub>5</sub>	2.03	276	514	142	287	Water, acids	—

Potassium chlorate	KClO <sub>3</sub>	2.3	368	dec	—	—	Charcoal, sulfur, and phosphorous	b
Potassium nitrate	KNO <sub>3</sub>	2.1	334	400	—	—	Friction, contact with organics	b
Potassium nitrite	KNO <sub>2</sub>	1.9	388	dec	—	—	Friction, impact	
Sodium	Na	0.97	98	890	—	—	Moisture	a
Sodium hydride	NaH	0.9	800	—	—	—	Water, oxidizers	a
Sodium nitrate	NaNO <sub>3</sub>	2.3	307	379	—	—	Contact with organics	b
Sodium nitrite	NaNO <sub>2</sub>	2.17	271	318	—	—	Contact with organics	b
Sodium styrene sulfonate	C <sub>8</sub> H <sub>7</sub> SO <sub>3</sub> Na	—	225 (dec)	—	—	462	Hot surfaces, sparks	a, b, c
Sulfur	S/S <sub>8</sub>	2.07	115	445	207	232	Heat	a, d
Triphenylboron	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> B	—	136	347	—	220	Water (produces benzene), heat	a, b, c, d

*Note:* dec = decomposes; sub = sublimes

<sup>a</sup> Dry chemical extinguisher.

<sup>b</sup> H<sub>2</sub>O.

<sup>c</sup> CO<sub>2</sub>.

<sup>d</sup> Foam.

<sup>e</sup> Wet sand.

<sup>f</sup> Chlorinated hydrocarbons.

## COMPOUNDS THAT ARE REACTIVE WITH WATER

The following is a partial listing of families of compounds that are known to have reactivity with water.<sup>1</sup> Depending upon the specific compound, the reaction can be rapid and even violent, or simply slow hydrolysis.

## REFERENCES

1. Bretherick, L., Urban, P.G., and Pitt, M.J., *Bretherick's Handbook of Reactive Chemical Hazards: An Indexed Guide to Published Data*, 6th ed., Butterworths, London, 1999.

Acid anhydrides  
Acyl halides  
Alkali metals  
Alkylaluminum derivatives  
Alkylmagnesium derivatives  
Alkyl nonmetal halides  
Complex anhydrides  
Metal halides (some)  
Metal oxides (some)  
Nonmetal halides and their oxides  
Nonmetal oxides

## PYROPHORIC COMPOUNDS: COMPOUNDS THAT ARE REACTIVE WITH AIR

The following listing provides the classes of compounds, with some examples, that can undergo spontaneous reaction upon exposure to air.<sup>1,2</sup> In some cases, the reaction is vigorous, while in others, the reaction is more subdued or will only occur if other conditions (such as temperature, humidity, or a reactive surface) are present. Check the literature for more specific information.

### REFERENCES

1. Bretherick, L., Urben, P.G., and Pitt, M.J., *Bretherick's Handbook of Reactive Chemical Hazards: An Indexed Guide to Published Data*, 6th ed., Butterworths, London, 1999.
2. Pyrophoric Materials, [www.safety.science.tamu.edu/pyrophorics.html](http://www.safety.science.tamu.edu/pyrophorics.html), Texas A&M University, 2003.

Alkali metals<sup>a</sup>

(sodium, potassium, potassium/sodium alloy, lithium/tin alloys)

Alkylaluminum derivatives

(diethylaluminum hydride)

Alkylated metal alkoxides

(diethylethoxyaluminum)

Alkylboranes

Alkylhaloboranes

(bromodimethyl borane)

Alkylhalophosphines

Alkylhalosilanes

Alkyl metals

Alkyl nonmetal hydrides

Boranes

(diborane)

Carbonyl metals

(pentacarbonyl iron, octacarbonyl dicobalt, nickel carbonyl)

Complex acetylides

Complex hydrides

(diethylaluminum hydride)

Finely divided metals<sup>a</sup>

(calcium, zirconium)

Haloacetylene derivatives

Hexamethylnitrato dialuminum salts

Metal hydrides

(germane, sodium hydride, lithium aluminum hydride)

Nonmetal hydrides

Some nonmetal (organic) halides

(dichloro(methyl)silane)

Spent hydrogenation catalysts

(can be especially hazardous because of adsorbed hydrogen; for example, Raney nickel)

White phosphorus

<sup>a</sup> Note that the reactivity depends on the particle size and the ease with which oxides are formed on the metal surface.

## VAPOR PRESSURE OF MERCURY

The following table provides data on the vapor pressure of mercury, useful for assessing and controlling the hazards associated with the use of mercury, for example, as an electrode.<sup>1</sup>

### REFERENCES

1. Lide, D.R., Ed., *CRC Handbook of Chemistry and Physics*, 83rd ed., CRC Press, Boca Raton, FL, 2002.

Vapor Pressure of Mercury					
Temperature (°C)	Vapor Pressure (mmHg)	Vapor Pressure (Pa)	Temperature (°C)	Vapor Pressure (mmHg)	Vapor Pressure (Pa)
0	0.000185	0.0247	28	0.002359	0.3145
10	0.000490	0.0653	30	0.002777	0.3702
20	0.001201	0.1601	40	0.006079	0.8105
22	0.001426	0.1901	50	0.01267	1.689
24	0.001691	0.2254	100	0.273	36.4
26	0.002000	0.2666			

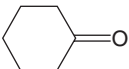

## FLAMMABILITY HAZARDS OF COMMON LIQUIDS

The following table lists relevant data regarding the flammability of common organic liquids.<sup>1</sup>

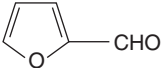
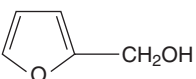
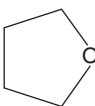
### REFERENCES

1. Turner, C.F. and McCreery, J.W., *The Chemistry of Fire and Hazardous Materials*, Allyn and Bacon, Boston, 1981.

**Flammability Hazards of Common Liquids**

Solvent	Formula	Specific Gravity	Boiling Point (°C)	Flash Point (°C)	Auto-ignition Point (°C)	How to Extinguish Fires
Acetaldehyde	CH <sub>3</sub> CHO	0.8	21	-38	185	a, b, c
Acetone	(CH <sub>3</sub> ) <sub>2</sub> CO	0.8	57	-18	538	a, b
Acetonitrile	CH <sub>3</sub> C≡N	0.79	82	6	—	a, c, d
Acetylacetone	CH <sub>3</sub> COCH <sub>2</sub> COCH <sub>3</sub>	1.0	139	41	—	a, b, c
Acrolein	CH <sub>2</sub> =CHCHO	0.8	53	-26	277	a, b, c
Acrylonitrile	CH <sub>2</sub> =CH-CHC≡N	0.81	77	0	481	a, c, d
Allylamine	CH <sub>2</sub> =CHCH <sub>2</sub> NH <sub>2</sub>	0.8	53	-29	374	a, b
Amylmercaptan	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> SH	0.8	127	18	—	a, b
Aniline	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	1.0	184	70	768	a, b, c Use masks
Anisole	C <sub>6</sub> H <sub>5</sub> OCH <sub>3</sub>	1.0	154	52	—	a, b, c
Benzaldehyde	C <sub>6</sub> H <sub>5</sub> CHO	1.1	179	65	192	a, b, c
Benzene	C <sub>6</sub> H <sub>6</sub>	0.88	79	-11	563	a, b, c
Bromine	Br <sub>2</sub>	3.0	59	—	—	CO <sub>2</sub> (never H <sub>2</sub> O)
<i>n</i> -Butyl alcohol	<i>n</i> -C <sub>4</sub> H <sub>9</sub> OH	0.8	117	29	366	a, b, c
<i>t</i> -Butylperacetate	CH <sub>3</sub> CO(O <sub>2</sub> )C(CH <sub>3</sub> ) <sub>3</sub>	—	—	<27	—	b, c
<i>t</i> -Butylperbenzote	C <sub>6</sub> H <sub>5</sub> CO(O <sub>2</sub> )C(CH <sub>3</sub> ) <sub>3</sub>	>1.0	112	88	8	a, b, c
<i>n</i> -Butyraldehyde	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CHO	0.8	76	7	230	a, b, c
Carbon disulfide	CS <sub>2</sub>	1.3	47	-30	100	b,d Use masks
Crotonaldehyde	CH <sub>3</sub> CH=CHCHO	0.9	104	13	232	a, b, c
Cumene hydroperoxide	C <sub>6</sub> H <sub>5</sub> C(CH <sub>3</sub> ) <sub>2</sub> O <sub>2</sub> H	1.0	153	175	—	a, b, c
Cyclohexanone		0.9	156	43	420	a, b, c
Diacetyl	(CH <sub>3</sub> CO) <sub>2</sub>	1.0	88	27	—	a, b, c
Diethanolamine	(HOCH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> NH	1.1	269	152	662	b, c
Diethylene glycol diethylether	CH <sub>3</sub> (CH <sub>2</sub> OCH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	0.9	189	83	—	a Halons
Diethylether	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	0.7	34	-45	180	a, b Halons
Diethylketone	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> CO	0.8	101	13	452	a, b, c
Dimethyl sulfate	(CH <sub>3</sub> ) <sub>2</sub> SO <sub>4</sub>	1.3	188	83	188	a, b, c, d
Dimethyl sulfide	(CH <sub>3</sub> ) <sub>2</sub> S	0.8	37	-18	206	b, c
1,4-Dioxane		1.0	101	2	180	a, b, c
Ethanol	C <sub>2</sub> H <sub>5</sub> OH	0.8	78	13	423	a, b, c
Ethylacetone (2-pentanone)	CH <sub>3</sub> COCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	0.8	102	7	504	a, b, c
Ethylamine	C <sub>2</sub> H <sub>5</sub> NH <sub>2</sub>	0.7	31	-18	384	a, b, c

# Flammability Hazards of Common Liquids (continued)

Solvent	Formula	Specific Gravity	Boiling Point (°C)	Flash Point (°C)	Auto-ignition Point (°C)	How to Extinguish Fires
Ethylenediamine	$\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$	0.9	117	34	385	a, b, c
Ethyleneglycol	$\text{HOCH}_2\text{CH}_2\text{OH}$	1.1	198	111	413	a, b, c, d
Formaldehyde	$\text{HCHO}$	1.0	99	88	427	a, b, c
Furfural		1.2	162	60	316	a, b, c, d
Furfuryl alcohol		1.1	171	75	491	a, b, c
Gasoline	$\text{C}_8\text{H}_{18}$ (isomers)	<1.0	38–218	–43	257	a, b, c
Hexylamine	$\text{C}_6\text{H}_{13}\text{NH}_2$	0.8	132	29	—	a, b
Isopropanol	$(\text{CH}_3)_2\text{CHOH}$	0.8	82	12	399	b, c
Isopropyl ether	$((\text{CH}_3)_2\text{CH})_2\text{O}$	0.7	68	–28	443	a, b
Kerosene	$\text{CH}_4$ series mixture	<1.0	149–316	38–71	229	a, b, c
Methanol	$\text{CH}_3\text{OH}$	0.8	65	11	464	a, b
Methylamine (aq)	$\text{CH}_3\text{NH}_2$	0.7	31	–18	384	a, b, c
Methylaniline	$\text{CH}_3\text{NHC}_6\text{H}_5$	0.8	151	49	533	a, b
Methylethyl ketone	$\text{CH}_3\text{COCH}_2\text{CH}_3$	0.8	79	–6	516	a, b, c
Methylethyl ketone peroxide	$\text{C}_8\text{H}_{16}\text{O}_4$	—	—	63	—	a, b
Naphtha (mixture)	—	0.8–0.9	149–216	38–46	227–496	a, b, c
Paraldehyde	$(\text{CH}_3\text{CHO})_3$ , cyclic	1.0	124	36	238	a, b, c
2-Pentanone	See Ethylacetone	—	—	—	—	—
3-Pentenitrile	$\text{CH}_3\text{CH}=\text{CHCH}_2\text{C}\equiv\text{N}$	0.83	14.5	40	—	b, c, d
Peracetic acid	$\text{CH}_3\text{COOOH}$	1.2	105	40	—	a, b, c
Petroleum ether	—	<0.7	38–79	<0	288	a, b, c
Propionaldehyde	$\text{CH}_3\text{CH}_2\text{CHO}$	0.8	49	8	207	a, b, c
Propylamine	$\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$	0.7	49	–37	318	a, b, c
Propylene glycol	$\text{CH}_3\text{CHOHCH}_2\text{OH}$	1.0	188	99	421	a, b
Sulfur chloride	$\text{S}_2\text{Cl}_2$	1.7	138	118	234	b, c
Sulfuryl chloride	$\text{SO}_2\text{Cl}_2$	1.7	69	—	—	a, b, c
Tetrahydrofuran		0.9	60	–17	321	a, b, c
Thionyl chloride	$\text{SOCl}_2$	1.6	79	—	—	—
Toluene	$\text{C}_6\text{H}_5\text{CH}_3$	0.87	111	4	510	a, b, c
Triethanolamine	$(\text{HOCH}_2\text{CH}_2)_3\text{N}$	1.1	360	179	—	b, c, d
Triethylamine	$(\text{C}_2\text{H}_5)_3\text{N}$	0.7	89	7	—	a, b, c
Xylene (o-)	$\text{C}_6\text{H}_4(\text{CH}_3)_2$	0.88	144	32	463	a, b, c
Xylene (m-)	$\text{C}_6\text{H}_4(\text{CH}_3)_2$	0.86	139	29	527	a, b, c
Xylene (p-)	$\text{C}_6\text{H}_4(\text{CH}_3)_2$	0.86	138	39	529	a, b, c



## ABBREVIATIONS USED IN THE ASSESSMENT AND PRESENTATION OF LABORATORY HAZARDS

The following abbreviations are commonly encountered in presentations of laboratory and industrial hazards. The reader is urged to consult the reference<sup>1</sup> for additional information.

### REFERENCES

1. Furr, A.K., ed., *CRC Handbook of Laboratory Safety*, 5th ed., CRC Press, Boca Raton, FL, 2000.

**CC** Closed Cup; method for the measurement of the flash point. With this method, Sample vapors are not allowed to escape as they can with the open cup method. Because of this, flash points measured with the CC method are usually a few degrees lower than those measured with the OC. The choice between CC and OC is dependent on the (usually ASTM) standard method chosen for the test.

**COC** Cleveland Open Cup, see Open Cup.

**IDLH** Immediately Dangerous to Life and Health; the maximum concentration of chemical contaminants, normally expressed as parts per million (ppm, mass/mass), from which one could escape within 30 minutes without a respirator, and without experiencing any escape impairing (severe eye irritation) or irreversible health effects. Set by NIOSH. Note that this term is also used to describe electrical hazards.

**LEL** Lower Explosion Limit; the minimum concentration of a chemical in air at which detonation can occur.

**LFL** Lower Flammability Limit; the minimum concentration of a chemical in air at which flame propagation occurs.

**MSDS** Material Safety Data Sheet; a (legal) document that must accompany any supplied chemical that provides information on chemical content, physical properties, hazards, and treatment of hazards. The MSDS should be considered only a minimal source of information, and cannot replace additional information available in other, more comprehensive sources.

**NOEL** No Observed Effect Level; the maximum dose of a chemical at which no signs of harm are observed. This term can also be used to describe electrical hazards.

**OC** Open Cup; also called Cleveland Open Cup. This refers to the test method for determining the flash point of common compounds. It consists of a brass, aluminum or stainless steel cup, a heater base to heat the cup, a thermometer in a fixture and a test flame applicator. The flash point is the lowest temperature at which a material will form a flammable mixture with air above its surface. The lower the flash point, the easier it is to ignite.

**PEL** Permissible Exposure Level; an exposure limit that is published and enforced by OSHA as a legal standard. The PEL may be expressed as a time-weighted-average (TWA) exposure limit (for an 8 hour workday), a 15-minute short term exposure limit (STEL), or a ceiling (C, or CEIL, or TLV-C).

**REL** Recommended Exposure Level; average concentration limit recommended for up to a 10-hour workday during a 40-hour workweek, by NIOSH.

**RTECS** Registry of Toxic Effects of Chemical Substances; a database maintained by the National Institute of Occupational Safety and Health (NIOSH). The goal of the database, is to include data on all known toxic substances, along with the concentration at which toxicity is known to occur. There are approximately 140,000 compounds listed.

**STEL** Short Term Exposure Level; an exposure limit for a short term, 15 minute, exposure that cannot be exceeded during the workday, enforced by OSHA as a legal standard. Short term exposures below the STEL level generally will not cause irritation, chronic or reversible tissue damage, or narcosis.

**TLV** Threshold Limit Value; guidelines suggested by the American Conference of Governmental Industrial Hygienists to assist industrial hygienists with limiting hazards of chemical exposures in the workplace.

**TLV-C** Threshold Limit Ceiling Value; an exposure limit which should not be exceeded under any circumstances.

**TWA** Time-weighted average concentration for a conventional 8-hour workday and a 40 hour workweek. It is the concentration to which it is believed possible that nearly all workers can be exposed without adverse health effects.

**UEL** Upper Explosion Limit; the maximum concentration of a chemical in air at which detonation can occur.

**UFL** Upper Flammability Limit; the maximum concentration of a chemical in air at which flame propagation can occur.

**WEEL** Workplace Environmental Exposure Limit; set by the American Industrial Hygiene Association (AIHA).

Some abbreviations that are sometimes used on material safety data sheets, and in other sources, are ambiguous. The most common meanings of some of these vague abbreviations are provided below, but the reader is cautioned that these are only suggestions:

**EST** Established; estimated

**MST** Mist

**N/A, NA** Not applicable

**ND** None determined; not determined

**NE** None established; not established

**NEGL** Negligible

**NF** None found; not found

**N/K, NK** Not known

**N/P, NP** Not provided

**SKN** Skin

**TS** Trade secret

**UKN** Unknown

## CHEMICAL CARCINOGENS

The following table contains data on chemicals often used in the analytical laboratory, which have come under scrutiny for their suspected or observed carcinogenicity.<sup>1-7</sup> The reader is advised to use these tables with care, as there is a great deal of volatility in the classifications as new data become available. It is suggested that the reader maintain a current file of data from the appropriate regulatory agencies, and to err on the side of caution.

## REFERENCES

1. Partial List of Selected Carcinogens, [www.people.memphis.edu/~ehas/carcinogen.html](http://www.people.memphis.edu/~ehas/carcinogen.html), 2003.
2. Ruth, J.H., Odor thresholds and irritation levels of several chemical substances: a review, *Am. Ind. Hyg. Assoc. J.*, 47, A-142, 1986.
3. Chemical Carcinogens, New Jersey Department of Health and Senior Services, Occupational Health Service, [www.state.nj.health.eoh](http://www.state.nj.health.eoh), 2003.
4. Hazard Database: List of Carcinogens [www.ephb.nw.ru/~spirov/carcinogen\\_1st.html](http://www.ephb.nw.ru/~spirov/carcinogen_1st.html), 2003.
5. *Tenth Report on Carcinogens*, U.S. Department of Health and Human Services, Public Health Service, National Toxicology Program, National Institute of Environmental Health Sciences, Research Triangle Park, Durham, NC, 2002.
6. EHP Online, [www.ehp.niehs.nih.gov/roc/toc10.html](http://www.ehp.niehs.nih.gov/roc/toc10.html), 2003.
7. *NIOSH Pocket Guide to Chemical Hazards*, National Institute of Occupational Safety and Health, Washington, D.C., 1997.

### Chemical Carcinogens

Chemical Name	CAS Number	IARC <sup>a</sup>	NTP <sup>b</sup>	OSHA <sup>c</sup>	Odor Low, mg/m <sup>3</sup>	Irritating Concentration, mg/m <sup>3</sup>
Acetaldehyde	75-07-0	2B	Y			
Acetamide	60-35-5	2B				
2-Acetylaminofluorene	53-96-3		Y	Y		
Acrylamide	79-06-1	2A	Y			
Acrylonitrile	107-13-1	2B	Y	*	8.1	
Actinomycin D	50-76-0	2B				
Adriamycin	23214-92-8	2A	Y			
Aflatoxins	1402-68-2	1	#			
2-Aminoanthraquinone	117-79-3		Y			
p-Aminoazobenzene	60-09-3	2B				
4-Aminobiphenyl	92-67-1	1	#	Y		
1-Amino-2-methyl anthraquinone	82-28-0		Y			
o-Aminoazotoluene	97-56-3	2B	Y			
2-Aminonaphthalene	91-59-8	1	#	*		
Ammonium dichromate	7789-09-5	2B				
Amitrole	61-82-5	2B	Y			
Androgenic steroids		2A				
o-Anisidine	90-04-0	2B	Y			
o-Anisidine hydrochloride	134-29-2	2B	Y			
Antimony trioxide	1309-64-4	2B				
Aramite	140-57-8	2B				
Arsenic compounds (certain)		1	#	*		
Arsenic, metal	7440-38-2	1	#	*		
Asbestos	1332-21-4	1	#	*		
Auramine, technical	2465-27-2	2B				
Azathioprine	446-86-6	1	#			
Aziridine		2B				

**Chemical Carcinogens (continued)**

Chemical Name	CAS Number	IARC <sup>a</sup>	NTP <sup>b</sup>	OSHA <sup>c</sup>	Odor Low, mg/m <sup>3</sup>	Irritating Concentration, mg/m <sup>3</sup>
Benz[a]anthracene	56-55-3	2A	Y			
Benzene	71-43-2	1	#	*	4.5	9000
Benzidine	92-87-5	1	#	Y		
Benzidine-based dyes		2A	Y			
Benzo[b]fluoranthene	205-99-2	2B	Y			
Benzo[j]fluoranthene	205-82-3	2B	Y			
Benzo[k]fluoranthene	207-08-9	2B	Y			
Benzofuran	271-89-6	2B				
Benzo[a]pyrene	50-32-8	2A	Y			
Benzotrichloride	98-07-7		Y			
Benzyl violet 4B	1694-09-3	2B				
Beryllium	7440-41-7	1	Y	Y		
Beryllium sulfate	13510-49-1	1				
Beryllium compounds (certain)		1	Y	A		
<i>N,N</i> -Bis-(2-chloro-ethyl)-2-naphthylamine (chlornaphazine)	494-03-1	1				
Bis-chloroethyl nitrosourea (BCNU)	154-93-8	2A	Y			
Bis-chloromethyl ether (BCME)	542-88-1	1	#	Y		
Bromodichloromethane	75-27-4	2B	Y			
1,3-Butadiene	106-99-0	2A	Y	D	0.352	
1,4-Butanediol dimethanesulfonate	55-98-1	1	#			
Butylated hydroxyanisole	25013-16-5	2B	Y			
Butyrolactone, beta	3068-88-0	2B				
Cadmium	7440-43-9	1	Y	*		
Caffeic acid	331-39-5	2B				
Carbon black	1333-86-4	2B		d		
Carbon tetrachloride	56-23-5	2B	Y	d	60–300	
Catechols		2B				
Chlorambucil	305-03-3	1	#			
Chloramphenicol	56-75-7	2A				
Chlordane	57-74-9	2B				
Chordecone (kepone)		2B				
Chlorinated toluenes, alpha		2A				
<i>p</i> -Chloroaniline		2B				
1-(2-Chloroethyl)-3-cyclohexyl-1-nitrosourea (CCNU)	13010-47-4	1	#			
Chloroform	67-66-3	1B	Y	d	250	20,480
Chloromethyl methyl ether	107-30-2		#	a		
1-Chloro-2-methylpropene	513037-1	2B				
3-Chloro-2-methylpropene	563-47-3		Y			
Chlorophenols		C			0.0189	6801.18
4-Chloro- <i>o</i> -phenylenediamine	95-83-0	2B	Y			
Chloroprene	126-99-8	2B		b		
<i>p</i> -Chloro- <i>o</i> -toluidine	95-69-2	2A	Y			
Chlorozotocin	54749-90-5	2A	Y			
Chromium	7440-47-3	1	#			
Chromium compounds (certain)		1	#			
Chromium (VI) ions	18540-29-9	1	#			
Chrysene	218-01-9					
Cisplatin	15663-27-1	2A	Y			
Cobalt and compounds	7440-48-4	2B				
<i>p</i> -Cresidine	120-71-8	2B	Y			
Cupferron	135-20-6		Y			

**Chemical Carcinogens (continued)**

<b>Chemical Name</b>	<b>CAS Number</b>	<b>IARC<sup>a</sup></b>	<b>NTP<sup>b</sup></b>	<b>OSHA<sup>c</sup></b>	<b>Odor Low, mg/m<sup>3</sup></b>	<b>Irritating Concentration, mg/m<sup>3</sup></b>
Cycasin	14901-08-7	2B	B			
Cyclophosphamide	50-18-0	1	#			
Dacarbazine	4342-03-4	2B	Y			
DDT	50-29-3	2B	Y	d	5.0725	
<i>N,N'</i> -Diacetylbenzidine	613-35-4	2B				
2,4-Diaminoanisole	615-05-4	2B				
2,4-Diaminoanisole sulfate	39156-41-7		Y			
4,4'-Diaminodiphenyl ether	101-80-4	2B				
2,4-Diaminotoluene	95-80-7	2B	Y			
Dibenz[a,h]acridine	226-36-8	2B	Y			
Dibenz[a,j]acridine	224-42-0	2B	Y			
Dibenz[a,h]anthracene	53-70-3	2A	Y			
7H-Dibenzo[c,g]carbazole	194-59-2	2B	Y			
Dibenzo[a,e]pyrene	192-65-4	2B	Y			
Dibenzo[a,e]pyrene	189-64-0	2B	Y			
Dibenzo[a,i]pyrene	189-55-9	2B	Y			
Dibenzo[a,l]pyrene	191-30-0	2B	Y			
1,2-Dibromo-3-chloropropane (DBCP)	96-12-8	2B	Y	*	0.965	1.93
<i>p</i> -Dichlorobenzene	106-46-7	2A	Y			
3,3'-Dichlorobenzidine	91-94-1	2B	Y	*		
3,3'-Dichlorobenzidine salts				*		
3,3'-Dichloro-4,4'-diaminodiphenyl ether	28434-86-8	2B				
1,2-Dichloroethane	107-06-2	2B	Y			
Dichloromethane	75-09-2	2B	Y	*		
1,3-Dichloropropene	542-75-6	2B	Y			
Di-(2-ethylhexyl) phthalate		2B	Y			
1,2-Diethylhydrazine	1615-80-1	2B	Y			
Dieldrin	60-57-1			Y		
Dienoestrol	84-17-3	1				
Diepoxybutane	1464-53-5		B			
Di-(2,3-ethylhexyl) phthalate	117-81-7	2B	Y			
Diethylstilbestrol (DES)	56-53-1	1	#			
Diethyl sulfate	64-67-5	2A	Y			
Dihydrosafrole	94-58-6	2B				
1,8-Dihydroxyanthraquinone	117-10-2		Y			
Diisopropyl sulfate	2973-10-6	2B				
3,3'-Dimethoxybenzidine	119-90-4	2B	Y			
4-Dimethylaminoazobenzene	60-11-7	2B	Y	Y		
2,6-Dimethylaniline	87-62-7	2B				
3,3'-Dimethylbenzidine	119-93-7	2B	Y			
Dimethylcarbamoyl chloride	79-44-7	2A	Y			
1,1-Dimethyl hydrazine	57-14-7	2B	Y	d		
Dimethyl sulfate	77-78-1	2A	Y	d		
Dinitrofluoranthrene, isomers		2B				
1,8-Dinitropyrene	42397-65-9	2B				
2,4-Dinitrotoluene	121-14-2	2B				
2,6-Dinitrotoluene	606-20-2	2B				
1,4-Dioxane	123-91-1	2B	Y		0.0108	792
Direct black 38, technical	1937-37-7		Y			
Direct blue 6, technical	2602-46-2		Y			
Direct brown 95, technical	16071-86-6	1				
Disperse blue 1	2475-45-8	2B	Y			
Epichlorohydrin	106-89-8	2A	Y	d	50	335

**Chemical Carcinogens (continued)**

Chemical Name	CAS Number	IARC <sup>a</sup>	NTP <sup>b</sup>	OSHA <sup>c</sup>	Odor Low, mg/m <sup>3</sup>	Irritating Concentration, mg/m <sup>3</sup>
1,2-Epoxybutane		2B				
Erionite	12510-42-8	1	#			
Ethinylestradiol	57-63-6	1				
Ethyl acrylate	140-88-5	2B	Y			
Ethylene dibromide (EDB)	106-93-4	2A	Y		76.8	
Ethylene dichloride (EDC)	107-06-2	2B	Y	Y	24	
Ethyleimine	151-56-4			Y	4	200
Ethylene oxide	72-21-8	1	Y	*	520	
Ethylene thiourea	96-45-7	2B	Y			
Ethyl methanesulfonate	62-50-0	2B	Y			
<i>N</i> -Ethyl- <i>N</i> -nitrosourea		2A				
Formaldehyde	50-00-0	2A	Y	*	1.47	1.50
2-(2-Furyl)-3-(5-nitro-2-furyl) acrylamide	3688-53-7	2B				
2-(2-Formyl-hydrazino)-4-(5-nitro-2-furyl) thiazole	3570-75-0	2B				
Furan	110-00-9	2B	Y			
Gyromitrin	16568-02-8	1				
Hexachlorobenzene	118-74-1	2B	Y			
Hexachloroethane	67-72-1	2B	Y			
Hexamethyl phosphoramidate	680-31-9	2B	Y			
Hydrazine	302-01-2	2B	Y	Y	3	
Hydrazine sulfate	10034-93-2		Y			
Hydrazobenzene	122-66-7		Y			
Indeno [1,2,3-cd] pyrene	193-39-5	2B				
Isoprene	78-79-5	2B				
Lead (II) acetate	301-04-2	2B	Y	*		
Lead chromate	7758-97-6		#			
Lead phosphate	7446-27-7	2B	B	*		
Lindane (and other hexachlorocyclohexane isomers)	58-89-9		Y	Y		
Melphalan	148-82-3	1	#			
Merphalan	531-76-0	2B				
Mestranol	72-33-3	1				
2-Methylaziridine		2B	Y			
Methylazoxy-methanol acetate	592-62-1	2B				
Methyl chloromethyl ether				Y		
5-Methylchrysene	3697-24-3	2B				
4,4'-Methylenebis (2-chloroaniline (MOCA)	101-14-4	2A	Y			
4,4'-Methylenebis ( <i>N,N</i> -dimethyl-benzenamine)	69522-43-6		Y			
4,4'-Methylene dianiline	101-77-9	2B	Y			
Methyl bromide	74-83-9			Y	80	
Methyl chloride	74-87-3	1			21	1050
Methyl hydrazine	60-34-4	1			1.75	
Methyl iodide	74-88-4			Y		21,500
Methylmercury compounds		2B				
Methyl methanesulfonate	66-27-3	2A				
<i>N</i> -Methyl- <i>N</i> -nitrosourea	684-93-5	2A				
<i>N</i> -Methyl- <i>N</i> -nitrosourethane		2B				
Methylthiouracil	56-04-2	2B				
Metronidazole	443-48-1	2B	Y			
Michler's ketone	90-94-8		Y			
Mirex	2385-85-5	2B	Y			

**Chemical Carcinogens (continued)**

<b>Chemical Name</b>	<b>CAS Number</b>	<b>IARC<sup>a</sup></b>	<b>NTP<sup>b</sup></b>	<b>OSHA<sup>c</sup></b>	<b>Odor Low, mg/m<sup>3</sup></b>	<b>Irritating Concentration, mg/m<sup>3</sup></b>
Mustard gas	505-60-2	1	#		0.015	
α-Naphthylamine	134-32-7			Y		
β-Naphthylamine	91-59-8	1	#	Y		
Nickel carbonyl	13463-39-3	1	Y		0.21	
Nickel	7440-02-0	2B				
Nickel compounds (certain)		1	#	*		
Nickel, metallic and inorganic compounds	7440-02-0	1	#			
Nitrlotriacetic acid	139-13-9		b			
5-Nitroacenaphthene	602-87-9	2B				
2-Nitroanisole	91-23-6	2B	Y			
5-Nitro- <i>o</i> -anisidine	99-59-2		b			
Nitrobenzene	98-95-3	2B				
4-Nitrobiphenyl	92-93-3			Y		
6-Nitrochrysene	7496-02-8	2B	Y			
Nitrofen	1836-75-5	2B	Y			
Nitrofluorene	607-57-8	2B				
Nitrogen mustard	55-86-7	2A	Y			
Nitrogen mustard <i>N</i> -oxide	126-85-2	2B				
2-Nitropropane	79-46-9	2B	Y		17.5	
1-Nitropyrene	5522-43-0	2B	Y			
4-Nitropyrene	57835-92-4	2B	Y			
<i>N</i> -Nitroso- <i>N</i> -ethyl urea	759-73-9		Y			
<i>N</i> -Nitroso- <i>N</i> -methyl urea	684-93-5		Y			
<i>N</i> -Nitroso-di- <i>n</i> -butyl amine	924-16-3	2B	Y			
<i>N</i> -Nitroso- <i>n</i> -propyl amine	621-64-7	2B	Y			
<i>N</i> -Nitroso-dimethyl amine	62-75-9	2A	Y	Y		
<i>N</i> -Nitroso-diethanol amine	1116-54-7	2B	Y			
<i>N</i> -Nitroso-diethyl-amine	55-18-5	2A	Y			
<i>N</i> -Nitroso-dimethyl amine	62-75-9	2A	Y	Y		
<i>p</i> -Nitroso-di-phenylamine	156-10-5		Y			
<i>N</i> -Nitroso-di- <i>n</i> -propylamine	621-64-7		Y			
<i>N</i> -Nitroso- <i>N</i> -ethyl urea	759-73-9		Y			
<i>N</i> -Nitroso- <i>N</i> -methyl urea	684-93-5		Y			
<i>N</i> -Nitrosomethyl-vinylamine	4549-40-0	2B	Y			
<i>N</i> -Nitrosomorpholine	59-89-2	2B	Y			
<i>N</i> -Nitrososornicotine	16543-55-8	2B	Y			
<i>N</i> -Nitrosopiperidine	100-75-4	2B	Y			
<i>N</i> -Nitrosopyrrolidine	930-55-2	2B	Y			
<i>N</i> -Nitrososarcosine	13256-22-9	2B	Y			
Norethisterone	68-22-4		Y			
Oestradiol-17B	50-28-2	1				
Oestrone	53-16-7	1				
4,4'-Oxydianiline	101-80-4		Y			
Oxymetholone	434-07-1		Y			
Phenacetin	62-44-2	2A	Y			
Phenazopyridine	94-78-0	2B	Y			
Phenobarbitol	50-06-6	2B				
Phenazopyridine hydrochloride	136-40-3	2B	Y			
Phenoxyacetic acid derivatives		1		Y		
Phenoxybenzamine hydrochloride	63-92-3	2B	Y			
Phenyl glycidyl ether	122-60-1	2B				
<i>N</i> -Phenyl-β-naphthylamine	135-88-6	1				
Phenylhydrazine	100-63-0			Y		
Phenytoin	57-41-0	2B	Y			

**Chemical Carcinogens (continued)**

Chemical Name	CAS Number	IARC <sup>a</sup>	NTP <sup>b</sup>	OSHA <sup>c</sup>	Odor Low, mg/m <sup>3</sup>	Irritating Concentration, mg/m <sup>3</sup>
Phenytion, sodium salt	630-93-3		Y			
Polybrominated biphenyls (PBBs)	36355-01-8	2B	Y			
Polychlorinated biphenyls (PCBs)		2B	Y	*		
Polychlorinated camphenes		2A				
Polychlorophenols		2B				
Polycyclic aromatic compounds		2A	Y			
Potassium bromate	7758-01-2	2B				
Potassium chromate	7789-00-6	1				
Potassium dichromate	7778-50-9	1				
Procarbazine	671-16-9	2A	Y			
Procarbazine hydrochloride	366-70-1	2A	Y			
Propane sultone	1120-71-4	2B	Y			
β-Propiolactone	57-57-8	2B	Y	Y		
Propyleneimine	75-55-8			#		
Propylene oxide	75-56-9	2B	Y			
Propylthiouracil	51-52-5	2B	Y			
Reserpine	50-55-5		Y			
Saccharin	81-07-2		Y			
Safrole	94-59-7	2B	Y		1.4586	
Selenium sulfide	7446-34-6		Y	*		
Silica crystalline (respirable)		1	Y			
Streptozotocin	18883-66-4	2B	Y			
Strontium chromate	7789-06-2		#			
Sulfallate	95-06-7	2B	Y			
2,3,7,8-Tetrachlorodibenzo- <i>p</i> -dioxin (TCDD)	1746-01-6	1	Y			
1,1,2,2-Tetrachloroethane	79-34-5			*	21	1302
Tetrachloroethylene	127-18-4	2	Y	*	31.3561	710.2
Tetrafluoroethylene		2B				
Tetranitromethane	509-14-8	2B	Y			
Thioacetamide	62-55-5	2B	Y			
4,4'-Thiodianiline	139-65-1	2B				
Thiourea	62-56-6	2B	Y			
Thorium dioxide	1314-20-1		#			
<i>p</i> -Tolidine	119-93-7		Y			
<i>o</i> -Toluidine	95-53-4	2B	Y			
<i>p</i> -Toluidine		2B	Y			
<i>o</i> -Toluidine hydrochloride	636-21-5		Y			
<i>p</i> -Toluidine	106-49-0		Y			
Toxaphene	8001-35-2	2B	Y	*	2.366	
Treosulfan	299-75-2	1				
1,1,2-Trichloroethane	79-00-5			*		
Trichloroethylene	79-01-6	2A		*		
2,4,6-Trichlorophenol	88-06-2	2B	BY			
Tris (aziridinyl)- <i>p</i> -benzoquinone (triaziquinone)	68-76-8	1	#			
Tris (2,3-dibromopropyl) phosphate	126-72-7	2A	Y			
Tryptophan P1	62450-06-0	2B				
Tryptophan P2	62450-07-1	2B				
Trypan blue	72-57-1	2B				
Uracil mustard	66-75-1	2B				
Urethane	51-79-6	2B	Y			
Vinyl acetate	108-05-4	2B				



### Chemical Carcinogens (continued)

Chemical Name	CAS Number	IARC <sup>a</sup>	NTP <sup>b</sup>	OSHA <sup>c</sup>	Odor Low, mg/m <sup>3</sup>	Irritating Concentration, mg/m <sup>3</sup>
Vinyl bromide	593-60-2	2A				
Vinyl chloride	75-01-4	1	#	*		
Vinyl cyclohexene diepoxide	106-87-6	2B	Y			
Vinyl fluoride	75-02-5	2A				
Vinylidene chloride	75-35-4	2A			2000	
Vinylidene fluoride (monomer)	75-38-7	2A				

<sup>a</sup> Compiled from monographs of the International Agency for Research on Cancer (IARC) (part of the United Nations World Health Organization), as data becomes available. Classifications are as follows:

- 1 Known human carcinogen
- 2A Probable human carcinogen
- 2B Possible human carcinogen

<sup>b</sup> Compiled from data of the National Toxicology Program (NTP) whose reports are updated every 2 years (Branch of the U.S. Department of Health and Human Services). Classifications are as follows:

- Y Reasonably anticipated to be human carcinogen
- # Known human carcinogen

<sup>c</sup> Compiled from data of the Occupational Safety and Health Administration (OSHA), with standards set by the legislative process (part of the U.S. Department of Labor). Classifications are as follows:

Note: a = alcohol foam; b = carbon dioxide; c = dry chemical extinguisher; d = water.

Y Possibly a human carcinogen

\* Substance for which OSHA has promulgated expanded health standards that govern health concerns in addition to carcinogenesis

## ORGANIC PEROXIDES

The following ethers have been tested for the potential to undergo conversion to peroxides.<sup>1,2</sup>

### REFERENCES

1. Ramsey, J.B. and Aldridge, F.T., Removal of peroxides from ethers with cerous hydroxide, *J. Am. Chem. Soc.*, 77, 2561, 1955.
2. Furr, A.K., Ed., *CRC Handbook of Laboratory Safety*, 5th ed., CRC Press, Boca Raton, FL, 2000.

Organic Peroxides	
Ether	Quantities of Peroxides Found
Allyl ethyl ether	Moderate
Allyl phenyl ether	Moderate
Benzyl ether	Moderate
Benzyl <i>n</i> -butyl ether	Moderate
<i>o</i> -Bromophenetole	Very small
<i>p</i> -Bromophenetole	Very small
<i>n</i> -Butyl ether	Moderate
<i>t</i> -Butyl ether	Moderate
<i>p</i> -Chloroanisole	Very small
<i>o</i> -Chloroanisole	Very small
Bis-(2-ethoxyethyl) ether (diethylene glycol diethyl ether)	Considerable
2-(2-Butoxyethoxy) ethanol (diethylene glycol mono- <i>n</i> -butyl ether)	Moderate
1,4-Dioxane	Moderate
Diphenyl ether	Moderate
Ethyl ether <sup>a</sup>	Very small
Ethyl ether <sup>b</sup>	Considerable
Ethyl ether <sup>c</sup>	Moderate
Isopropyl ether	Considerable
<i>o</i> -Methylanisole	Very small
<i>m</i> -Methylphenetole	Very small
Phenetole	Very small
Tetrahydrofuran	Moderate

<sup>a</sup> Obtained from sealed can of anhydrous ether, analytical reagent, immediately after opening.

<sup>b</sup> Obtained from a partially filled tin can (well-stopped) containing the same grade of anhydrous ether as that described in note a, but allowed to stand for an appreciable time.

<sup>c</sup> From a galvanized iron container used for dispensing ether.

## TESTING REQUIREMENTS FOR PEROXIDIZABLE COMPOUNDS

Because some compounds form peroxides more easily or faster than others, prudent practices require testing the supply on hand in the laboratory on a periodic basis. The following list provides guidelines on test scheduling.<sup>1</sup> The peroxide hazard of the compounds listed in group 1 is on the basis of time in storage. The compounds in group 2 present a peroxide hazard primarily due to concentration, mainly by evaporation of the liquid. The compounds listed in group 3 are hazardous because of the potential of peroxide-initiated polymerization. When stored as liquids, the peroxide formation may increase, and therefore these compounds should be treated as group 1 peroxidizable compounds.

## REFERENCES

1. Ringen, S., *Environmental Health and Safety Manual: Chemical Safety*, Section 4-50, University of Wyoming, Laramie, June 2000.

### Group 1 — Test every 3 months

- Divinyl acetylene
- Isopropyl ether
- Potassium
- Sodium amide
- Vinylidene chloride

### Group 2 — Test every 6 months

- Acetal
- Cumene
- Cyclohexene
- Diacetylene
- Dicyclopentadiene
- Diethyl ether
- Dimethyl ether
- 1,4-Dioxane
- Ethylene glycol dimethyl ether (glyme)
- Methyl acetylene
- Methyl isobutyl ketone
- Methyl cyclopentane
- Tetrahydrofuran
- Tetrahydronaphthalene (tetralin)
- Vinyl ethers

### Group 3 — Test every 12 months

- Acrylic acid
- Acrylonitrile
- Butadiene
- Chloroprene
- Chlorotrifluoroethylene
- Methyl methacrylate
- Styrene
- Tetrafluoroethylene
- Vinyl acetate
- Vinyl acetylene
- Vinyl chloride
- Vinyl pyridine

## TESTS FOR THE PRESENCE OF PEROXIDES

Peroxides may be detected qualitatively with one of the following test procedures:<sup>1</sup>

### REFERENCES

1. Gordon, A.J. and Ford, R.A., *The Chemist's Companion*, John Wiley & Sons, New York, 1972.

#### **Ferrithiocyanate test:**

Reagent preparation:

1. Add 9 g of  $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$  to 50 ml of 18% (vol/vol)  $\text{HCl}_{(\text{aq})}$ .
2. Add 1 to 3 mg of granular Zn.
3. Add 5 g of NaSCN.
4. After the red color fades, add an additional 12 g of NaSCN; decant, leaving unreacted Zn.
5. Upon mixing this reagent with a peroxide-containing liquid, the colorless solution will produce a red color, the result of the conversion of ferrothiocyanate to ferrithiocyanate. This test is very sensitive and can be used to detect peroxides at a concentration of 0.001% (mass/mass).

#### **Potassium iodide test:**

Reagent preparation:

1. Make a 10% (mass/mass) solution of KI in water.
2. Upon mixing this reagent with a peroxide-containing liquid, a yellow color will appear within 1 min.

#### **Acidic iodide test:**

Reagent preparation:

1. To 1 ml of glacial acetic acid, add 100 mg of KI or NaI.
2. Upon mixing this reagent with an equal volume of a peroxide-containing liquid, a yellow coloration will appear. The color will appear dark or even brown if the peroxide concentration is very high.

#### **Perchromate test:**

Reagent preparation:

1. Dissolve 1 mg of  $\text{Na}_2\text{Cr}_2\text{O}_7$  in 1 ml of water; add a drop of dilute  $\text{H}_2\text{SO}_{4(\text{aq})}$ .
2. Upon mixing this reagent with a peroxide-containing liquid, a blue color will develop in the organic layer, indicating of the formation of the perchromate ion.

## CHARACTERISTICS OF CHEMICAL-RESISTANT MATERIALS

The following table provides guidance in the selection of materials that provide some degree of chemical resistance for common laboratory tasks.<sup>1</sup>

### REFERENCES

1. Furr, A.K., Ed., *CRC Handbook of Laboratory Safety*, 5th ed., CRC Press, Boca Raton, FL, 2000

### Physical Characteristics of Chemical-Resistant Materials

Material	Abrasion Resistance	Cut Resistance	Flexibility	Heat Resistance	Ozone Resistance	Puncture Resistance	Tear Resistance	Relative Cost
Butyl rubber	F	G	G	E	E	G	G	High
Chlorinated polyethylene (CPE)	E	G	G	G	E	G	G	Low
Natural rubber	E	E	E	F	P	E	E	Medium
Nitrile–butadiene rubber (NBR)	E	E	E	G	F	E	G	Medium
Neoprene	E	E	G	G	E	G	G	Medium
Nitrile rubber (nitrile)	E	E	E	G	F	E	G	Medium
Nitrile rubber + polyvinylchloride (nitrile + PVC)	G	G	G	F	E	G	G	Medium
Polyethylene	F	F	G	F	F	P	F	Low
Polyurethane	E	G	E	G	G	G	G	High
Polyvinyl alcohol (PVA)	F	F	P	G	E	F	G	Very high
Polyvinyl chloride (PVC)	G	P	F	P	E	G	G	Low
Styrene–butadiene rubber (SBR)	E	G	G	G	F	F	F	Low
Viton	G	G	G	G	E	G	G	Very high

*Note:* E = excellent; G = good; F = fair; P = poor.

## SELECTION OF PROTECTIVE LABORATORY GARMENTS

The following table provides guidance in the selection of special protective garments that are used in the laboratory for specific tasks.<sup>1</sup>

### REFERENCES

1. Mount Sinai School of Medicine Personal Protective Equipment Guide, [www.mssm.edu/biosafety/policies](http://www.mssm.edu/biosafety/policies), 2003.

Selection of Protective Laboratory Garments		
Material	Type of Garment	Common Use
Cotton/natural fiber/blends	Coveralls; lab coats; sleeve protectors; aprons	For dry dusts, particulates, and aerosols
Tyvek	Coveralls; lab coats; sleeve protectors; aprons; hoods	For dry dusts and aerosols
Saranax/Tyvek SL	Coveralls; lab coats; sleeve protectors; aprons; hoods; level B suits	Aerosols, liquids, solvents
Polyethylene	Barrier gowns; aprons	Body fluids
Polypropylene	Clean room suits; coveralls; lab coats	For dry dusts, nontoxic particulates
Polyethylene/Tyvek (QC)	Coveralls; aprons; lab coats; shoe covers	Moisture, solvents
Polypropylene	Coveralls; lab coats; shoe covers; caps; clean room suits	Nontoxic particulates, dry dusts
Tychem BR; Tychem TK	Full level A and level B suits	Highly toxic particulates, dry dusts
CPF	Full level A and level B suits; splash suits	Highly toxic chemicals, gases, aerosols
PVC	Full level A suits	Highly toxic chemicals, gases, aerosols

## PROTECTIVE CLOTHING LEVELS

In the U.S., OSHA defines various levels of protective clothing and sets parameters that govern their use with chemical spills and in environments where chemical exposure is a possibility. A summary of the definitions is provided below.<sup>1</sup>

### REFERENCES

1. Chemical Protective Clothing, in *OSHA Technical Manual*, OSHA, 2003, Section VIII, chap. 1.

#### Level A:

- Vapor-protective suit (meets NFPA 1991); pressure-demand, full-face SCBA; inner chemical-resistant gloves; chemical-resistant safety boots; two-way radio communication
- Protection provided: highest available level of respiratory, skin, and eye protection from solid, liquid, and gaseous chemicals
- Used when: the chemical(s) have been identified and have high level of hazards to respiratory system, skin, and eyes; substances are present with known or suspected skin toxicity or carcinogenicity; operations must be conducted in confined or poorly ventilated areas
- Limitations: protective clothing must resist permeation by the chemical or mixtures present

#### Level B:

- Liquid splash-protective suit (meets NFPA 1992); pressure-demand, full-face-piece SCBA; inner chemical-resistant gloves; chemical-resistant safety boots; two-way radio communication
- Protection provided: provides same level of respiratory protection as level A, but somewhat less skin protection; liquid splash protection is provided, but not protection against chemical vapors or gases
- Used when: the chemical(s) have been identified but do not require a high level of skin protection; the primary hazards associated with site entry are from liquid and not vapor contact
- Limitations: protective clothing items must resist penetration by the chemicals or mixtures present

#### Level C:

- Support function protective garment (meets NFPA 1993); full-face-piece, air-purifying, canister-equipped respirator; chemical-resistant gloves and safety boots; two-way communications system
- Protection provided: the same level of skin protection as level B, but a lower level of respiratory protection; liquid splash protection but no protection to chemical vapors or gases
- Used when: contact with site chemical(s) will not affect the skin; air contaminants have been identified and concentrations measured; a canister is available that can remove the contaminant; the site and its hazards have been completely characterized
- Limitations: protective clothing items must resist penetration by the chemical or mixtures present; chemical airborne concentration must be less than IDLH (immediate danger to life or health) levels; the atmosphere must contain at least 19.5% oxygen
- Not acceptable for chemical emergency response

#### Level D:

- Coveralls, safety boots/shoes, safety glasses, or chemical splash goggles
- Protection provided: no respiratory protection, minimal skin protection
- Used when: the atmosphere contains no known hazard; work functions preclude splashes, immersion, potential for inhalation, or direct contact with hazard chemicals
- Limitations: the atmosphere must contain at least 19.5% oxygen
- Not acceptable for chemical emergency response

Optional items may be added to each level of protective clothing. Options include items from higher levels of protection, as well as hard hats, hearing protection, outer gloves, a cooling system, etc.



## SELECTION OF LABORATORY GLOVES

The following table provides guidance in the selection of protective gloves for laboratory use.<sup>1-4</sup> If protection from more than one class of chemical is required, double gloving should be considered.

### REFERENCES

1. Garrod, A.N., Martinez, M., and Pearson, J., Proud, A., and Rimmer, D.A., Exposure to preservatives used in the industrial pre-treatment of timber, *Ann. Occup. Hyg.*, 43, 543, 1999.
2. Garrod, A.N., Phillips, A.M., and Pemberton, J.A., Potential exposure of hands inside protective gloves—a summary of data from non-agricultural pesticide surveys, *Ann. Occup. Hyg.*, 45, 55, 2001.
3. Mickelsen, R.L. and Hall, R.C., A breakthrough time comparison of nitrile and neoprene glove materials produced by different glove manufacturers, *Am. Ind. Hyg. Assoc. J.*, 48, 941, 1987.
4. OSHA, Federal Register, Vol. 59, No. 66, 16334–16364, 29 CFR 1910, 1994.

**Selection of Laboratory Gloves**

Glove Material	Resistant to
Viton	PCBs, chlorinated solvents, aromatic solvents
Viton/butyl	Acetone, toluene, aromatics, aliphatic hydrocarbons, chlorinated solvents, ketones, amines, aldehydes
SilverShield and 4H (PE/EVAL)	Morpholine, vinyl chloride, acetone, ethyl ether, many toxic solvents and caustics
Barrier	Wide range of chlorinated solvents, aromatic acids
PVA	Ketones, aromatics, chlorinated solvents, xylene, MIBK, trichloroethylene; <i>do not use with water/aqueous solutions</i>
Butyl	Aldehydes, ketones, esters, alcohols, most inorganic acids, caustics, dioxane
Neoprene	Oils, grease, petroleum-based solvents, detergents, acids, caustics, alcohols, solvents
PVC	Acids, caustics, solvents, grease, oil
Nitrile	Oils, fats, acids, caustics, alcohols
Latex	Body fluids, blood, acids, alcohols, alkalis
Vinyl	Body fluids, blood, acids, alcohols, alkalis
Rubber	Organic acids, some mineral acids, caustics, alcohols; not recommended for aromatic solvents, chlorinated solvents

## SELECTION OF RESPIRATOR CARTRIDGES AND FILTERS

Respirators are sometimes desirable or required when performing certain tasks in the chemical analysis laboratory. There is a standardized color code system used by all manufacturers for the specification and selection of the cartridges and filters that are used with respirators. The following table provides guidance in the selection of the proper cartridge using the color code.

Selection of Respirator Cartridges and Filters	
Color Code	Application
Gray	Organic vapors, ammonia, methylamine, chlorine, hydrogen chloride, and sulfur dioxide or hydrogen sulfide (for escape only) or hydrogen fluoride or formaldehyde
Black	Organic vapors, not to exceed regulatory standards
Yellow	Organic vapors, chlorine, chlorine dioxide, hydrogen chloride, hydrogen fluoride, sulfur dioxide, or hydrogen sulfide (for escape only)
White	Chlorine, hydrogen chloride, hydrogen chloride, hydrogen fluoride, sulfur dioxide, or hydrogen sulfide (for escape only)
Green	Ammonia and methylamine
Orange	Mercury and/or chlorine
Purple	Solid and liquid aerosols and mists
Purple + gray	Organic vapors, ammonia, methylamine, chlorine, hydrogen chloride, and sulfur dioxide or hydrogen sulfide (for escape only) or hydrogen fluoride or formaldehyde; solid and liquid aerosols and mists
Purple + black	Organic vapors, and solid and liquid aerosols and mists
Purple + yellow	Organic vapors, chlorine, chlorine dioxide, hydrogen chloride, hydrogen fluoride, sulfur dioxide, or hydrogen sulfide (for escape only); solid and liquid aerosols and mists
Purple + white	Chlorine, hydrogen chloride, hydrogen chloride, hydrogen fluoride, sulfur dioxide, or hydrogen sulfide (for escape only); solid and liquid aerosols and mists
Purple + green	Ammonia, methylamine, and solid and liquid aerosols and mists

In addition to the cartridges specified in the table, particulate filters are available that can be used alone or in combination.

## EFFECTS OF ELECTRICAL CURRENT ON THE HUMAN BODY

The following table provides information on the effects of electrical shock on the human body.<sup>1</sup> The table lists current values in milliamperes. The voltage is an important consideration as well because of the relationship with resistance:

$$I = V/R$$

where I is the current, V is the voltage, and R is the resistance. The presence of moisture can significantly decrease the resistance of the human skin, and thereby increase the hazard of an electrical shock. The current difference between a barely noticeable shock and a lethal shock is only a factor of 100. In individuals with cardiac problems, the difference may be lower.

## REFERENCES

1. Furr, A.K., Ed., *CRC Handbook of Laboratory Safety*, 5th ed., CRC Press, Boca Raton, FL, 2000.

Effects of Electrical Current on the Human Body	
Current (mA)	Reaction
1	Perception level; a faint tingle
5	Slight shock felt; disturbing but not painful; average person can let go; however, vigorous involuntary reactions to shocks in this range can cause accidents
6–25 (women) 9–30 (men)	Painful shock; muscular control is lost; called freezing or “let-go” range <sup>a</sup>
50–150	Extreme pain, respiratory arrest, severe muscular contractions; individual normally cannot let go unless knocked away by muscle action; death is possible
1000–4300	Ventricular fibrillation (the rhythmic pumping action of the heart ceases); muscular contraction and nerve damage occur; death is most likely
10,000+	Cardiac arrest, severe burns, and probable death

<sup>a</sup> The person may be forcibly thrown away from the contact if the extensor muscles are excited by the shock.

## ELECTRICAL REQUIREMENTS OF COMMON LABORATORY DEVICES

The following table lists some common laboratory devices along with the current and power requirements for the operation of the device.<sup>1</sup> This information is important to consider when instrumentation is being installed, relocated, or used on the same circuit. Common 120-V circuits in laboratories are typically rated at 10 or 15 A. Note that the current draw often spikes to a high level in first few microseconds after a device is energized. This is especially true for devices that have electric motors.

## REFERENCES

1. Furr, A.K., Ed., *CRC Handbook of Laboratory Safety*, 5th ed., CRC Press, Boca Raton, FL, 2000.

Electrical Requirements of Common Laboratory Devices		
Instrument	Current (A)	Power (W)
Balance (electronic)	0.1–0.5	12–60
Biological safety cabinet	15	1800
Blender	3–15	400–1800
Centrifuge	3–30	400–6000
Chromatograph	15	1800
Computer (PC)	2–4	400–6000
Freeze dryer	20	4500
Fume hood blower	5–15	600–1800
Furnace/oven	3–15	500–3000
Heat gun	8–16	1000–2000
Heat mantle	0.4–5	50–600
Hot plate	4–12	450–1400
Kjeldahl digester	15–35	1800–4500
Refrigerator/freezer	2–10	250–1200
Stills	8–30	1000–5000
Sterilizer	12–50	1400–12,000
Vacuum pump (mechanical)	4–20	500–2500
Vacuum pump (diffusion)	4	500

## CHAPTER 15

# Miscellaneous Tables

### CONTENTS

Unit Conversions

Mass and Volume-Based Concentration Units

Concentration Units Nomenclature

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## UNIT CONVERSIONS

The international system of units is described in detail in NIST Special Publication 811,<sup>1</sup> and lists of physical constants and conversions factors of selected unit conversions<sup>1-6</sup> are given in the following tables. The conversions are presented in matrix format when all of the units are of a convenient order of magnitude. When some of the unit conversions are of little value (such as the conversion between metric tons and grains), tabular form is followed, with the less useful units omitted.

## REFERENCES

1. Taylor, B.N., *Guide for the Use of the International System of Units*, National Institute of Standards and Technology (U.S.) Special Publication SP-811, 1995.
2. Chiu, Y., *A Dictionary for Unit Conversion*, School of Engineering and Applied Science, The George Washington University, Washington, D.C., 1975, p. 20052.
3. Lide, D.R., Ed., *CRC Handbook of Chemistry and Physics*, 83rd ed., CRC Press, Boca Raton, FL, 2002.
4. Bruno, T.J. and Svoronos, P.D.N., *CRC Handbook of Basic Tables for Chemical Analysis*, CRC Press, Boca Raton, FL, 1989.
5. Units description in dictionary, [www.rutgers.edu](http://www.rutgers.edu), 2003.
6. Kimball's Biology Page, [www.biology\\_pages.info](http://www.biology_pages.info), 2003.

Area		
Multiply	By	To Obtain
Square millimeters	0.00155	Square inches (U.S.)
	$1 \times 10^{-6}$	Square meters
	0.01	Square centimeters
	1.2732	Circular millimeters
Square centimeters	$1.196 \times 10^{-4}$	Square yards
	0.00108	Square feet
	0.15500	Square inches
	$1 \times 10^{-4}$	Square meters
	100	Square millimeters
Square kilometers	0.38610	Square miles (U.S.)
	$1.1960 \times 10^6$	Square yards
	$1.0764 \times 10^7$	Square feet
	$1 \times 10^6$	Square meters
	247.10	Acres (U.S.)
Square inches (U.S.)	0.00694	Square feet
	0.00077	Square yards
	$6.4516 \times 10^{-4}$	Square meters
	6.4516	Square centimeters
	645.15	Square millimeters
Square feet (U.S.)	$3.5870 \times 10^{-8}$	Square miles
	0.11111	Square yards
	144	Square inches
	0.09290	Square meters
	929.03	Square centimeters
	$2.2957 \times 10^{-5}$	Acres
Square miles	640	Acres
	$3.0967 \times 10^6$	Square yards
	$2.7878 \times 10^7$	Square feet
	2.5900	Square kilometers

### Density

kg/m <sup>3</sup>	g/cm <sup>3</sup>	lb/ft <sup>3</sup>
16.018	0.016018	1
1	0.001	0.062428
1000	1	62.428
2015.9	2.0159	125.85

### Enthalpy, Heat of Vaporization, Heat of Conversion, Specific Energies

kJ/kg, (J/g)	cal/g	Btu/lb
2.3244	0.55556	1
1	0.23901	0.43022
4.1840	1	1.8

### Length

Multiply	By	To Obtain
Angstroms	$1 \times 10^{-10}$	Meters
	$3.9370 \times 10^{-9}$	Inches (U.S.)
	$1 \times 10^{-4}$	Micrometers
	$1 \times 10^{-8}$	Centimeters
	0.1	Nanometers
Nanometers	$1 \times 10^{-9}$	Meters
	$1 \times 10^{-7}$	Centimeters
	10	Angstroms
Micrometers (μm)	$3.9370 \times 10^{-5}$	Inches (U.S.)
	$1 \times 10^{-6}$	Meters
	$1 \times 10^{-4}$	Centimeters
	$1 \times 10^4$	Angstroms
Millimeters	0.03937	Inches (U.S.)
	1000	Micrometers
Centimeters	0.39370	Inches (U.S.)
	$1 \times 10^4$	Micrometers (μm)
	$1 \times 10^7$	Nanometers
	$1 \times 10^8$	Angstroms
Meters	$6.2137 \times 10^{-4}$	Miles (statute)
	1.0936	Yards (U.S.)
	39.370	Inches (U.S.)
	$1 \times 10^9$	Millimicrons
	$1 \times 10^{10}$	Angstroms
	0.53961	Miles (nautical)
Kilometers	0.62137	Miles (statute)
	1093.6	Yards
	3280.8	Feet
	0.02778	Yards
Inches (U.S.)	2.5400	Centimeters
	$2.5400 \times 10^8$	Angstroms
	0.30480	Meters
Feet (U.S.)	30.480	Centimeters
	$5.6818 \times 10^{-4}$	Miles
Yards (U.S.)	0.91440	Meters
	91.440	Centimeters
	1.1516	Miles (statute)
Miles (nautical)	2026.8	Yards
	1.8533	Kilometers
	320	Rods
Miles (U.S. statute)	0.86836	Miles (nautical)
	1.6094	Kilometers
	1609.4	Meters

### Pressure

MPa	atm	Torr (mmHg)	bar	lb/in. <sup>2</sup> (psi)
$6.8948 \times 10^{-3}$	0.068046	51.715	$6.8948 \times 10^{-2}$	1
1	9.8692	7500.6	10.0	145.04
0.101325	1	760.0	1.01325	14.696
$1.3332 \times 10^{-4}$	$1.3158 \times 10^{-3}$	1	$1.332 \times 10^{-3}$	0.019337
0.1	0.98692	750.06	1	14.504

### Specific Heat, Entropy

$\text{kJ}/(\text{kg-K})$ , $\text{J}/(\text{g-K})$	Btu/(°R-lb)
4.184	1
1	0.23901

### Specific Volume

$\text{m}^3/\text{kg}$ , (l/g)	$\text{cm}^3/\text{g}$	$\text{ft}^3/\text{lb}$
0.062428	62.428	1
1	1000	16.018
0.001	1	0.016018

### Surface Tension

N/m	dyne/cm	lb/in.
175.13	$175.13 \times 10^3$	1
1	1000	$5.7102 \times 10^{-6}$
0.001	1	$5.7102 \times 10^{-3}$

### Temperature

T (rankine)	=	1.8T (kelvin)
T (celsius)	=	T (kelvin) – 273.15
T (fahrenheit)	=	T (rankine) – 459.67
T (fahrenheit)	=	1.8T (celsius) + 32

### Thermal Conductivity

$\text{mW}/(\text{cm-K})$	$\text{J}/(\text{sec-cm-K})$	$\text{cal}/(\text{sec-cm-K})$	Btu/(ft-h-°R)
17.296	0.017296	0.0041338	1
1	0.001	$2.3901 \times 10^{-4}$	0.057816
1000	1	0.23901	57.816
4184	4.184	1	241.90



### Velocity

Multiply	By	To Obtain
Feet per minute	0.01136	Miles per hour
	0.01829	Kilometers per hour
	0.5080	Centimeters per second
	0.01667	Feet per second
Feet per second	0.6818	Miles per hour
	1.097	Kilometers per hour
	30.48	Centimeters per second
	0.3048	Meters per second
	0.5921	Knots
Knots (U.K.)	1.0	Nautical miles per hour
	1.6889	Feet per second
	1.1515	Miles per hour
	1.8532	Kilometers per hour
	0.5148	Meters per second
Meters per second	3.281	Feet per second
	2.237	Miles per hour
	3.600	Kilometers per hour
Miles per hour	1.467	Feet per second
	0.4470	Meters per second
	1.609	Kilometers per hour
	0.8684	Knots

### Velocity of Sound

m/sec	ft/sec
0.3048	1
1	3.2808

### Viscosity

kg/(m-sec), (N-sec/m <sup>2</sup> , Pa-sec)	cP, (10 <sup>-2</sup> g/(cm-sec))	lb-sec/ft <sup>2</sup> , (slug/(ft-sec))	lb/(ft-sec)
1.48816	1488.16	0.31081	1
1	1000	0.020885	0.67197
0.001	1	2.0885 × 10 <sup>-5</sup>	6.7197 × 10 <sup>-4</sup>
47.881	4.7881 × 10 <sup>-4</sup>	1	32.175

# Volume

Multiply	By	To Obtain
Barrels (pet)	42	Gallons (U.S.)
	34.97	Gallons (U.K.)
Cubic centimeters	$10^{-3}$	Liters
	0.0610	Cubic inches
Cubic feet	28317	Cubic centimeters
	1728	Cubic inches
	0.03704	Cubic yards
	7.481	Gallons (U.S., liq.)
	28.317	Liters
Cubic inches	16.387	Cubic centimeters
	0.016387	Liters
	$4.329 \times 10^{-3}$	Gallons (U.S., liq.)
	0.01732	Quarts (U.S. liq.)
Gallons, imperial	277.4	Cubic inches
	1.201	U.S. gallons
	4.546	Liters
Gallons, U.S. (liquid)	231	Cubic inches
	0.1337	Cubic feet
	3.785	Liters
	0.8327	Imperial gallons
	128	Fluid ounces (U.S.)
Ounces, fluid	29.57	Cubic centimeters
	1.805	Cubic inches
Liters	0.2642	Gallons
	0.0353	Cubic feet
	1.0567	Quarts (U.S. liq.)
	61.025	Cubic inches
Quarts, U.S. (liquid)	0.0334	Cubic feet
	57.749	Cubic inches
	0.9463	Liters

### Mass (Weight)

Multiply	By	To Obtain
Milligrams	$2.2046 \times 10^{-6}$	Pounds (avoirdupois)
	$3.5274 \times 10^{-5}$	Ounces (avoirdupois)
	0.01543	Grains
	$1 \times 10^{-6}$	Kilograms
Micrograms	$1 \times 10^{-6}$	Grams
Grams	0.00220	Pounds (avoirdupois)
	0.03527	Ounces (avoirdupois)
	15.432	Grains
	$1 \times 10^6$	Micrograms
Kilograms	0.00110	Tons (short)
	2.2046	Pounds (avoirdupois)
	35.274	Ounces (avoirdupois)
	$1.5432 \times 10^4$	Grains
Grains	$1.4286 \times 10^{-4}$	Pounds (avoirdupois)
	0.00229	Ounces (avoirdupois)
	0.06480	Grams
	64.799	Milligrams
Ounces (avoirdupois)	$3.1250 \times 10^{-5}$	Tons (short)
	0.06250	Pounds (avoirdupois)
	437.50	Grains
	28.350	Grams
Pounds (avoirdupois)	$5 \times 10^{-4}$	Tons (short)
	16	Ounces (avoirdupois)
	7000	Grains
	0.45359	Kilograms
	453.59	Grams
Tons (short, U.S.)	2000	Pounds (avoirdupois)
	$3.200 \times 10^4$	Ounces (avoirdupois)
	907.19	Kilograms
Tons (long)	2240	Pounds (avoirdupois)
	1016	Kilograms
Tons (metric)	1000	Kilograms
	2205	Pounds (avoirdupois)
	1.102	Tons (short)

## MASS AND VOLUME-BASED CONCENTRATION UNITS

Because the mass of 1 l of water is approximately 1 kg, mg/l units of aqueous solution are nearly equal to ppm units. The precise equivalence is obtained by dividing by the density D:

$$\text{ppm} = (\text{mg/liter})/D$$

where the solution density is in g/cm<sup>3</sup>. Some sources will substitute specific gravity for density in the above equation. The specific gravity is the ratio of the solution density to that of the density of pure water at 4°C. Since the density of pure water at 4°C is 1 g/cm<sup>3</sup>, the specific gravity is equal to the solution density when expressed in metric units of g/cm<sup>3</sup>.

### Parts per Million

Parts per Million	vs.	Percent
1	=	0.0001
10	=	0.001
100	=	0.01
1000	=	0.1
10,000	=	1.0
100,000	=	10.0
1,000,000	=	100.0

### Parts per Billion

Parts per Billion	vs.	Percent
10	=	0.000001
100	=	0.00001
1000	=	0.0001
10,000	=	0.001
100,000	=	0.01
1,000,000	=	0.1

### Parts per Trillion

Parts per Trillion	vs.	Percent
100	=	$1 \times 10^{-8}$
10,000	=	0.000001
1,000,000	=	0.0001
100,000,000	=	0.01

## CONCENTRATION UNITS NOMENCLATURE

The following table provides guidance in the use of base 10 concentration units (presented in the three preceding tables), since there are differences in colloquial usage worldwide.

Concentration Units Nomenclature			
Number	Number of Zeros	Name (Scientific Community)	Colloquial Name (U.K., France, Germany)
1000	3	Thousand	Thousand
1,000,000	6	Million	Million
1,000,000,000	9	Billion	Milliard, or thousand million
1,000,000,000,000	12	Trillion	Billion
1,000,000,000,000,000	15	Quadrillion	Thousand billion

## MOLAR-BASED CONCENTRATION UNITS

Molarity,  $M$  (moles of solute)/(liters of solution)

Molality,  $m$  (moles of solute)/(kilograms of solvent)

Normality,  $N$  (equivalents\* of solute)/(liters of solution)

Formality,  $F$  (moles of solute)/(kilograms of solution)

\*Reaction dependent; based on the number of protons exchanged in a given reaction.

To convert from ppm to formality units:

$F = \text{ppm}/(1000 \text{ RMM})$ , where RMM is the relative molecular mass of the solute.

To convert from ppm to molality units:

$m = [\text{ppm}/(1000 \text{ RMM})] [1/(1 - \text{tds}/1,000,000)]$ , where tds is the total dissolved solids in ppm in the solution.

To convert from ppm to molarity units:

$M = [\text{ppm}/(1000 \text{ RMM})] \rho$ , where  $\rho$  is the solution density.

## PREFIXES FOR SI UNITS

Fraction	Prefix	Symbol
$10^{-1}$	deci	d
$10^{-2}$	centi	c
$10^{-3}$	milli	m
$10^{-6}$	micro	$\mu$
$10^{-9}$	nano	n
$10^{-12}$	pico	p
$10^{-15}$	femto	f
$10^{-18}$	atto	a

Multiple	Prefix	Symbol
10	deka	da
$10^2$	hecto	h
$10^3$	kilo	k
$10^6$	mega	M
$10^9$	giga	G
$10^{12}$	tera	T
$10^{15}$	peta	P
$10^{18}$	exa	E

## RECOMMENDED VALUES OF SELECTED PHYSICAL CONSTANTS

The following table provides some commonly used physical constants that are of value in thermodynamic and spectroscopic calculations.<sup>1,2</sup>

### REFERENCES

1. Lide, D.R., Ed., *CRC Handbook of Chemistry and Physics*, 83rd ed., CRC Press, Boca Raton, FL, 2002.
2. The NIST Reference on Constants, Units and Uncertainty, [www.nist.gov](http://www.nist.gov), 2003.

Recommended Values of Selected Physical Constants

Physical Constant	Symbol	Value
Avogadro constant	$N_A$	$6.02214199 \times 10^{23} \text{ mol}^{-1}$
Boltzmann constant	$k$	$1.3806503 \times 10^{-23} \text{ J K}^{-1}$
Charge to mass ratio	$e/m$	$-1.758820174 \times 10^{11} \text{ C kg}^{-1}$
Elementary charge	$e$	$1.602176462 \times 10^{-19} \text{ C}$
Faraday constant	$F$	$96,485.3415 \text{ C mol}^{-1}$
Molar gas constant	$R$	$8.314472 \text{ J mol}^{-1} \text{ K}^{-1}$
Ice point temperature	$T_{\text{ice}}$	$273.150 \text{ K}$ (exactly)
Molar volume of ideal gas (stp)	$V_m$	$2.2413996 \times 10^{-2} \text{ m}^3 \cdot \text{mol}^{-1}$
Permittivity of vacuum	$\epsilon_o$	$8.854188 \times 10^{-12} \text{ kg}^{-1} \text{ m}^{-3} \cdot \text{sec}^4 \cdot \text{A}^2 (\text{F} \cdot \text{m}^{-1})$
Planck constant	$h$	$6.62606876 \times 10^{-34} \text{ J} \cdot \text{sec}$
Standard atmosphere pressure	$p$	$101,325 \text{ N} \cdot \text{m}^{-2}$ (exactly)
Atomic mass constant	$m_u$	$1.66053873 \times 10^{-27} \text{ kg}$
Speed of light in vacuum	$c$	$299,792,458 \text{ m sec}^{-1}$ (exactly)

## STANDARDS FOR LABORATORY WEIGHTS

The following table provides a summary of the requirements for metric weights and mass standards commonly used in chemical analysis.<sup>1,2</sup> The actual specifications are under the jurisdiction of ASTM Committee E-41 on General Laboratory Apparatus and are the direct responsibility of subcommittee E-41.06, which deals with weighing devices. These standards do not generally refer to instruments used in commerce. Weights are classified according to type (either type I or type II), grade (S, O, P, or Q), and class (1 to 6). Information on these mass standards is presented to allow the user to make appropriate choices when using analytical weights for the calibration of electronic analytical balances, for making large-scale mass measurements (such as those involving gas cylinders), and in the use of dead-weight pressure balances.

## REFERENCES

1. *Annual Book of ASTM Standards*, ANSI/ASTM E617-97 Standard Specification for Laboratory Weights and Precision Mass Standards, Book of Standards Vol. 14.04, ASTM, 2003.
2. Battino, R. and Williamson, A.G., Single pan balances, buoyancy and gravity, or “a mass of confusion,” *J. Chem. Educ.*, 61, 51, 1984.

### Type: Classification by Design

**Type I:** One-piece construction; contains no added adjusting material; used for highest accuracy work

**Type II:** Can be of any appropriate and convenient design, incorporating plugs, knobs, rings, etc.; adjusting material can be added if it is contained so that it cannot become separated from the weight



## Standards for Laboratory Weights

### Grade: Classification by Physical Property

Grade S	Density:	7.7–8.1 g/cm <sup>3</sup> (for 50 mg and larger)
	Surface area:	Not to exceed that of a cylinder of equal height and diameter
	Surface finish:	Highly polished
	Surface protection:	None permitted
	Magnetic properties:	No more magnetic than 300 series stainless steels
	Corrosion resistance:	Same as 303 stainless steel
	Hardness:	At least as hard as brass
Grade O	Density:	7.7–9.1 g/cm <sup>3</sup> (for 1 g and larger)
	Surface area:	Same as grade S
	Surface finish:	Same as grade S
	Surface protection:	May be plated with suitable material such as platinum or rhodium
	Magnetic properties:	Same as grade S
	Corrosion resistance:	Same as grade S
	Hardness:	At least as hard as brass when coated; smaller weights at least as hard as aluminum
Grade P	Density:	7.2–10 g/cm <sup>3</sup> (for 1 g or larger)
	Surface area:	No restriction
	Surface finish:	Smooth; no irregularities
	Surface protection:	May be plated or lacquered
	Magnetic properties:	Same as grades S and O
	Corrosion resistance:	Surface must resist corrosion and oxidation
Grade Q	Hardness:	Same as grade O
	Density:	7.2–10 g/cm <sup>3</sup> (for 1 g or larger)
	Surface area:	Same as grade P
	Surface finish:	Same as grade P
	Surface protection:	May be plated, lacquered, or painted
	Magnetic properties:	No more magnetic than unhardened unmagnetized steel
	Corrosion resistance:	Same as grade P
	Hardness:	Same as grades O and P

**Tolerance: Classification by Deviation<sup>a</sup>**

Class 1			Class 2			Class 3		Class 4		Class 5		Class 6	
Grams	Individual Tolerance, mg	Group Tolerance, mg	Grams	Individual Tolerance, mg	Group Tolerance, mg	Grams	Tolerance, mg	Grams	Tolerance, mg	Grams	Tolerance, mg	Grams	Tolerance, mg
500	1.2	1.35	500	2.5	2.7	500	5.0	500	10	500	30	500	50
300	0.75		300	1.5		300	3.0	300	6.0	300	20	300	30
200	0.50		200	1.0		200	2.0	200	4.0	200	15	200	20
100	0.25		100	0.5		100	1.0	100	2.0	100	9	100	10
50	0.12	0.16	50	0.25	0.29	50	0.6	50	1.2	50	5.6	50	7
30	0.074		30	0.15		30	0.45	30	0.9	30	4.0	30	5
20	0.074		20	0.10		20	0.35	20	0.7	20	3.0	20	3
10	0.050		10	0.074		10	0.25	10	0.5	10	2.0	10	2
5	0.034	0.065	5	0.054	0.105					5	1.3	5	2
3	0.034		3	0.054						3	0.95	3	2
2	0.034		2	0.054						2	0.75	2	2
1	0.034		1	0.054						1	0.50	1	2

<sup>a</sup> In simple terms, the permitted deviation between the assigned nominal mass value of the weight and the actual mass of the weight. Verification of tolerance should be possible on reasonably precise equipment, without using a buoyancy correction, within the political jurisdiction or organizational bounds of a given weight specification.

### Applications for Weights and Mass Standards<sup>a</sup>

Application	Type	Grade	Class
Reference standards used for calibrating other weights	I	S	1, 2, 3, or 4 <sup>a</sup>
High-precision standards for calibration of weights and precision balances	I or II <sup>b</sup>	S or O <sup>b</sup>	1 or 2 <sup>c</sup>
Working standards for calibration and precision analytical work, dead-weight pressure balances	I or II <sup>b</sup>	S or O	2
Laboratory weights for routine analytical work	II	O	2 or 3
Built-in weights, high-quality analytical balances	I or II	S	2
Moderate precision laboratory balances	II	P	3 or 4
Dial scales and trip balances	II	Q	4 or 5
Platform scales	II	Q	5 or 6

<sup>a</sup> Primary standards are for reference use only and should be calibrated. Since the actual values for each weight are stated, close tolerances are neither required nor desirable.

<sup>b</sup> Type I and Grade S will have a higher constancy but will probably be higher priced.

<sup>c</sup> Since working standards are used for the calibration of measuring instruments, the choice of tolerance depends upon the requirements of the instrument. The weights are usually used at the assumed nominal values, and appropriate tolerances should be chosen.

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## THERMOCOUPLE REFERENCE VOLTAGES

The following table provides power series expansions for the most common types of thermocouples used in the laboratory for temperature measurement.<sup>1,2</sup> It is best to use the thermocouple voltages in gradient mode, with the temperature of interest referenced to an additional thermocouple junction at some known temperature.

## REFERENCES

1. Powell, R.L., Hall, W.J., Hyink, C.H., Sparks, L.L., Burns, G.W., Scroger, M.G., and Plumb, H.H., Thermocouple Reference Tables, based on IPTS-68, NBS Monograph 125, March 1974.
2. Benedict, R.P., *Fundamentals of Temperature Pressure and Flow Measurements*, 3rd ed., John Wiley & Sons, New York, 1984

### Type T Thermocouples, Copper/Constantan

Temperature Range (°C)	Exact Reference Voltage (mV), <i>E</i>
0–400	$+3.8740773840 \times 10 \times T$ $+3.3190198092 \times 10^{-2} \times T^2$ $+2.0714183645 \times 10^{-4} \times T^3$ $-2.1945834823 \times 10^{-6} \times T^4$ $+1.1031900550 \times 10^{-8} \times T^5$ $-3.0927581898 \times 10^{-11} \times T^6$ $+4.5653337165 \times 10^{-14} \times T^7$ $-2.7616878040 \times 10^{-17} \times T^8 \times 10^{-3}$

### Type J Thermocouples, Iron/Constantan

Temperature Range (°C)	Exact Reference Voltage (mV), <i>E</i>
0–760	$+5.0372753027 \times 10 \times T$ $+3.0425491284 \times 10^{-2} \times T^2$ $-8.5669750464 \times 10^{-5} \times T^3$ $+1.3348825725 \times 10^{-7} \times T^4$ $-1.7022405966 \times 10^{-10} \times T^5$ $+1.9416091001 \times 10^{-13} \times T^6$ $-9.6391844859 \times 10^{-17} \times T^7 \times 10^3$

### Type E Thermocouples, Chromel/Constantan

Temperature Range (°C)	Exact Reference Voltage (mV), <i>E</i>
0–1000	$+5.8695857799 \times 10 \times T$ $+4.3110945462 \times 10^{-2} \times T^2$ $+5.7220358202 \times 10^{-5} \times T^3$ $-5.4020668085 \times 10^{-7} \times T^4$ $+1.5425922111 \times 10^{-9} \times T^5$ $-2.4850089136 \times 10^{-12} \times T^6$ $+2.3389721459 \times 10^{-15} \times T^7$ $-1.1946296815 \times 10^{-18} \times T^8$ $+2.5561127497 \times 10^{-22} \times T^9 \times 10^{-3}$

### Type K Thermocouples, Chromel/Alumel

Temperature Range (°C)	Exact Reference Voltage (mV), <i>E</i>
0–1100	<p>(<i>d</i>) Type K thermocouples</p> $-1.8533063273 \times 10$ $+3.8918344612 \times 10 \times T$ $+1.6645154356 \times 10^{-2} \times T^2$ $-7.8702374448 \times 10^{-5} \times T^3$ $+2.2835785557 \times 10^{-7} \times T^4$ $-3.5700231258 \times 10^{-10} \times T^5$ $+2.9932909136 \times 10^{-13} \times T^6$ $-1.2849848789 \times 10^{-16} \times T^7$ $+2.2239974336 \times 10^{-20} \times T^8$ $+125 \exp \left( -\frac{1}{2} \left\{ \frac{T-127}{65} \right\}^2 \right) \times 10^{-3}$

## STANDARD CGA FITTINGS FOR COMPRESSED GAS CYLINDERS

The following table presents a partial list of gases and the CGA fittings that are required to use those gases when they are stored in, and dispensed from, compressed gas cylinders.<sup>1</sup>

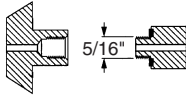
### REFERENCES

1. CGA Pamphlet V-1-87, American Canadian and Compressed Gas Association Standard for Compressed Gas Cylinder Valve Outlet and Inlet Connections, ANSI, B57.1; CSA B96, 1987.

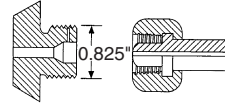
Standard CGA Fittings for Compressed Gas Cylinders	
Gas	Fitting
Acetylene	510
Air	346
Carbon dioxide	320
Carbon monoxide	350
Chlorine	660
Ethane	350
Ethylene	350
Ethylene oxide	510
Helium	580
Hydrogen	350
Hydrogen chloride	330
Methane	350
Neon	580
Nitrogen	580
Nitrous oxide	326
Oxygen	540
Sulfur dioxide	660
Sulfur hexafluoride	590
Xenon	580

The following graphic shows the geometry and dimensions of common CGA fittings for compressed gas cylinders.

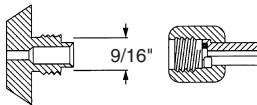
1. Reproduced from the CGA Pamphlet V-1-87, American Canadian and Compressed Gas Association Standard for Compressed Gas Cylinder Valve Outlet and Inlet Connections, ANSI, B57.1; CSA B96, 1987. With permission of the Compressed Gas Association



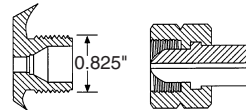
CONNECTION 110 - Lecture Bottle Outlet for Corrosive Gases - 5/16" - 32 RH INT., with Gasket



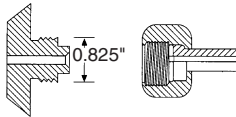
CONNECTION 326 - 0.825" - 14 RH EXT.



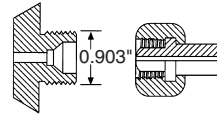
CONNECTION 170 - Lecture Bottle Outlet for Noncorrosive Gases 9/16" - 18 RH EXT. and 5/16" - 32 RH INT., with Gasket



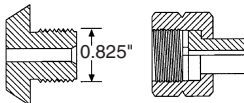
CONNECTION 350 - 0.825" - 14 LH EXT.



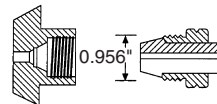
CONNECTION 320 - 0.825" - 14 RH EXT., with Gasket



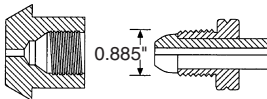
CONNECTION 540 - 0.903" - 14 RH EXT.



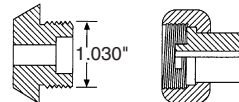
CONNECTION 330 - 0.825" - 14 LH EXT., with Gasket



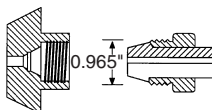
CONNECTION 590 - 0.956" - 14 LH INT.



CONNECTION 510 - 0.885" - 14 LH INT.



CONNECTION 660 - 1.030" - 14 RH EXT., with Gasket



CONNECTION 580 - 0.965" - 14 RH INT.

## GAS CYLINDER STAMPED MARKINGS

The graphic below describes the permanent, stamped markings that are used on high-pressure gas cylinders commonly found in analytical laboratories. Note that individual jurisdictions and institutions have requirements for marking the cylinder contents as well. These requirements are in addition to the stamped markings, which pertain to the cylinder itself rather than to the fill contents.

There are four fields of markings on cylinders that are used in the U.S., labeled 1 to 4 on the figure:

Field 1 — cylinder specifications

DOT stands for the U.S. Department of Transportation, the agency that regulates the transport and specification of gas cylinders in the U.S. The next entry, for example, 3AA, is the specification for the type and material of the cylinder. The most common cylinders are 3A, 3AA, 3AX, 3AAX, 3T, and 3AL. All but the last refer to steel cylinders, while 3AL refers to aluminum. The individual specifications differ mainly in chemical composition of the steel and the gases that are approved for containment and transport. 3T deals with large bundles of tube trailer cylinders. The next entry in this field is the service pressure, in psig.

Field 2 — serial number

This is a unique number assigned by the manufacturer.

Field 3 — identifying symbol

The manufacturer identifying symbol historically can be a series of letters or a unique graphical symbol. In recent years, the DOT has standardized this identification with the “M” number, for example, M1004. This is a number issued by DOT that identifies the cylinder manufacturer.

Field 4 — manufacturing data

The date of manufacture is provided as a month and year. With this date is the inspector’s official mark, for example, H. In recent years, this letter has been replaced with an IA number, for example, IA02, pertaining to an independent agency that is approved by DOT as an inspector.

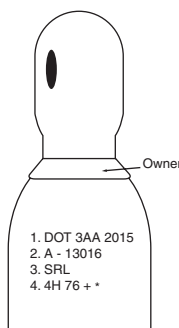
If + is present, the cylinder qualifies for an overfill of 10% in service pressure.

If \* is present, the cylinder qualifies for a 10-year rather than a 5-year retest interval.

Also stamped on the cylinder will be the retest dates. A cylinder must have a current (that is, within 5 or 10 years) test stamp. On the collar of the cylinder, the owner of the cylinder may be stamped.

## REFERENCES

1. *Hazardous Materials: Requirements for Maintenance, Requalification, Repair and Use of DOT Specification Cylinders*, 49 CFR Parts 107, 171, 172, 173, 177, 178, 179, and 180; Docket No. RSPA-01-10373 (HM-220D); RIN 2137-AD58, August 8, 2002.





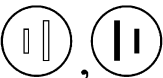
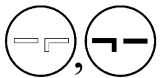
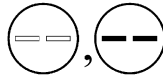

PLUG AND OUTLET CONFIGURATIONS FOR COMMON LABORATORY DEVICES

The following schematic diagrams show typical plug and outlet configurations used on common laboratory instruments and devices.<sup>1</sup> These figures will assist in identifying which circuits and capacities will be needed to operate different pieces of equipment.

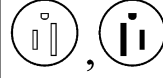
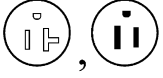
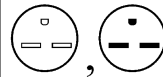
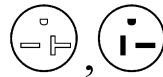
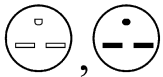
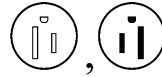
REFERENCES

1. *Plugs, Receptacles, and Connectors of the Pin and Sleeve Type for Hazardous Locations*, National Electrical Manufacturer Association, Standard FB2000, 2000.

2 pole, 2 wire

<div>Current</div> <div>Voltage</div>	<div>15 Amp</div> <div>R      P</div>	<div>20 Amp</div> <div>R      P</div>	<div>30 Amp</div> <div>R      P</div>	<div>50 Amp</div> <div>R      P</div>
125				
250				

2 pole, 3 wire (grounding)

<div>Current</div> <div>Voltage</div>	<div>15 Amp</div> <div>R      P</div>	<div>20 Amp</div> <div>R      P</div>	<div>30 Amp</div> <div>R      P</div>	<div>50 Amp</div> <div>R      P</div>
125				
250				

R = receptical  
P = plug